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THE CALCULATION OF RESONANT STATES OF
ATOMS AND MOLECULES BY QUASI-STATIONARY METHODS

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THE CALCULATION OF RESONANT STATES OF
ATOMS AND MOLECULES BY QUASI-STATIONARY METHODS

by

James Kendree Williams, Jr.

A Dissertation Presented to the
FACULTY OF THE GRADUATE SCHOOL
UNIVERSITY OF SOUTHERN CALIFORNIA

In Partial Fulfillment of the
Requirements for the Degree

DOCTOR OF PHILOSOPHY

(Chemical Physics)

August 1966

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This dissertation, written by

James Kendree Williams, Jr.

*under the direction of h^{is}.....Dissertation Com-
mittee, and approved by all its members, has
been presented to and accepted by the Graduate
School, in partial fulfillment of requirements
for the degree of*

DOCTOR OF PHILOSOPHY

DEDICATION

To my wife, Ann,
for patience, forbearance,
and silence beyond that expected of any wife.

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I would like to thank the United States Navy, the U. S. Naval Postgraduate School, and the Office of Naval Research for selecting me to participate in the Advanced Science Program and supporting my studies.

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CHAPTER I

INTRODUCTION

An important development in recent collision experiments has been the evidence of autoionizing compound negative ion states with lifetimes from 10^{-14} to 10^{-12} seconds; considerably shorter than the lifetimes of electronically excited states ($\sim 10^{-8}$ sec.). These compound states have been used to explain resonances in elastic scattering cross sections (Simpson and Fano, 1963), the onset of inelastic processes where no states of the target exist (Schulz and Philbrick, 1964; Chamberlain, 1965), forbidden transitions (Baranger and Guerjoy, 1957), and dissociative attachment (Schulz, 1958).

Most of the states observed in electron scattering experiments have energies lying slightly (0.1 - 1.0 eV) below known excited states of the target and the usual decay process is autoionization. Some specific examples of targets are hydrogen, helium, and the hydrogen molecule.

In hydrogen, the first excited state is $2S$ 2s or $2P$ 2p at 10.204 eV above the $1S$ 1s ground state. A resonance has been observed by Schulz (1964) at $9.75 \pm .15$ eV, just below the 2s or 2p energy.

At 19.3 eV above the ground state of the helium atom there is a sharp He^- resonance which is so well known that it is used for energy

scale calibration (Schulz, 1964; Simpson, Kuyatt, et al., 1965a; and many others). This is just below the $1,3S$ $1s2s$ states of helium at an average energy of 20.2 eV. Fano and Cooper (1965) have also discussed higher He^- resonances, such as the $2P$ $(2s)^2 2p$ at 57.1 eV and $2D$ $2s(sp)^2$ at 58.2 eV. These lie just below the $1S$ $(2s)^2$ and $3P$ $2s2p$ states at 57.9 and 58.4 eV respectively.

The pre-ionization states of helium can be considered as resonances of He^+ plus an electron. Madden and Codling (1964) have observed a set of these autoionizing levels, and Cooper, Fano and Prats (1963) have shown that they correspond to a series $(2snp+ns2p)^1P$, $n = 2, 3, \dots$ which converges to He^+ $2p$ (or $2s$) at 65.395 eV.

Kuyatt, Simpson and Mielczarek (1965b, 1966) have observed pairs of resonances starting about .9 eV below the $3,1\Pi_u$ states of the hydrogen molecule, and studied the isotope effect in HD and D_2 . In these experiments, spacings of levels were observed which correspond closely to the vibrational levels of the excited H_2 (HD, D_2) states, which seems to indicate that the third electron in the compound state became trapped in the field of the excited target state, but far enough away that it had little effect on the nuclear motion. Golden and Bandel (1965) report substantially the same result.

Various methods have been proposed and used for calculating the energies and wave functions of these compound states, particularly for scattering of electrons off atoms. The problem is that the normal variation method is inapplicable, as an infinity of states of the same symmetry and equal or lower energy exist for each resonance

consisting of the ground state of the target plus a free electron with the proper angular momentum and a continuum of energy values.

Fano (1961) and Burke and Schey (1962) have developed methods which actually deal with the scattering cross section. The Fano theory is particularly useful for analysis of line shape, while Burke and Schey use a close-coupling technique to calculate the cross section and study resonances as part of the total scattering problem.

Holþien (1958a,b), Holþien and Midtal (1965, 1966) Mandl and Herzenberg (1963, series), O'Malley and Geltman (1965), Taylor and this author (1965), and Lipsky and Russek (1966) have devised quasi-stationary methods for calculation of the energy and wave function of resonant states without predicting any of the features of the cross section except the approximate position of the resonance. Of the above, Taylor and Williams (1965, hereinafter denoted as TW) were the first to do calculations on systems other than two-electron atoms. The Taylor-Williams calculation was on the diatomic molecule H_2 plus an electron, and the results compared quite well with the experiments of Kuyatt, et al. (1965) and Golden and Bandel (1965). Since that time, Mandl and Herzenberg (1965) have done a parametrized calculation on the $^3\Sigma_u^+$ state of H_2 plus an electron with their modified Kapur-Peierls technique.

Taylor, Nazaroff, and Golebiewski (1966, hereinafter denoted as TNG), with the aid of the author, have presented a formal justification of the physical quasi-variation method of TW, and presented a complete quasi-stationary method for calculating the energy of resonances

which includes the TW method as a special case. This work also lists and classifies three types of resonances, including the examples above and two other types which will be discussed later.

Therefore, one of the aims of this work is to present the Taylor-Williams quasivariation method with its original physical arguments, and the formal justification of it as presented by TNG. This is done in Chapter II.

The second aim is to apply these methods to small diatomic molecules (in particular, H_2), calculating resonant states and comparing to electron scattering experiments (Chapter III, ff.).

Finally, in conjunction with the second aim, the diatomic molecule calculation methods of Harris (1960) Taylor and Harris (1963, series), and Taylor (1964) for bound states of six electrons or less have been revised to include the quasi-stationary methods, and have been extended to allow both bound and quasi-stationary calculations of energies and wave functions of larger diatomic systems. The latest revision, presented and discussed in the Appendices, can do calculations on up to twenty electrons.

CHAPTER II

THEORY

The formation, lifetime, and decay of the compound states mentioned above can only be described rigorously by wave packets composed of combinations of bound and continuum states of the $N+1$ electron system. The resonance is simply a highly localized wave packet which remains so for 10^{-14} to 10^{-12} seconds, so that with the proper restrictions, it can be treated as stationary during this time. This is similar to the treatment of electronically excited states as stationary by ignoring the light field interactions, where inclusion of the light field leads to decay in approximately 10^{-8} seconds.

Without any restrictions, a carefully executed variational calculation will lead to the conclusion that no compound states exist, since one can construct an infinite number of states of the same symmetry and equal or lower energy. Thus, even to apply the Hylleraas-Undheim procedure, treating the resonance as the m^{th} excited state, one would have to diagonalize an infinite secular determinant, taking the uppermost root as the resonance energy.

The original work of Taylor and Williams (TW, 1965) presented a quasi-variation method based on physical arguments for selecting the

proper restrictions so that valid results could still be obtained.

Briefly the method stated that if an $N+1$ electron bound state function could be guessed such that it nearly represented the physical situation, it would also closely resemble the proper linear combination of wave packets, and the matrix elements of interaction of this bound function with the infinite number of continuum functions would be so small compared to the bound-bound interactions that the infinite Hamiltonian matrix would be nearly numerically block diagonalized, separating the bound state in the continuum from its adjacent continuum.

The rules given for selecting these $N+1$ electron functions were that they must be doubly excited, autoionizing configurations, but with small autoionization probability in order to obtain long lifetimes. The small autoionization probability could be assured by selecting "weakly correlated" orbitals (i.e., orbitals having small $1/r_{ij}$ matrix elements) for the trial wave function. This choice of functions causes both the Hamiltonian and overlap matrices to be nearly block diagonal in the prescribed manner, since the double excitation produces an excited core which is orthogonal to the ground state of the target. Integration over the inner electrons will make the bound-continuum matrix elements small. Hence the total secular determinant is approximately block diagonalized into a finite part mixing multiply excited configurations of the compound state and an infinite part which can be ignored.

These arguments work quite well for certain types of resonances,

but considerable experimental evidence has appeared that there are other resonances which the quasi-variation method would not be able to calculate. Taylor, Nazarov, and Golebiewski (TNG, 1966) analyzed the experimental data and proposed that it could be explained by three types of resonance, which they classified as Type I Core-Excited, Type II Core-Excited, and Single Particle (hereinafter denoted by CE1, CE2, and SP, respectively).

The resonances of He, H, and H_2 discussed above, which lie 0.1 to 1.0 eV below excited states of the target, are CE1. They could be formed by the virtual process of the impinging electron exciting one of the electrons of the target and becoming trapped in the slight potential well left when the excited electron moves out of its way, with a resultant binding energy of 0.1 - 1.0 eV. The CE1 resonances are the ones which can be handled by the quasi-variation method, and the excitation of one of the target electrons explains the classification Core-Excited.

The potential well can be considered as being formed by additional amount of nuclear charge that the impinging electron sees when the excited core electron moves away.

One of the examples in many textbooks (for instance Messiah, 1961, Vol. I, p. 88) is the case of virtual levels of the square well potential, in which it is shown that if the walls of the finite ($V_0 = \infty$) well were made finite, "long-lived" localized wave packets (bound states in the continuum) can be formed only at those energies in the continuum of the well ($E > V_0$) at which bound states would have

existed had V_0 not been reduced to a finite value.

Based on this argument, TNG proposed the existence of CE2 resonances as virtual states of the potential well caused by core excitation. These resonances should be quite broad (short lived - width is inversely proportional to lifetime) compared to CE1, since they are adjacent to the continua of both the ground state of the target and the excited state of the target, and have no binding energy to provide stability. Experimental examples cited as indicative that CE2 resonances exist were the $\text{Hg}^- (5d^{10}6s6p^2) ^4P_{5/2}$ seen by Kuyatt, Simpson, and Mielczarek (1965) at 4.89 eV, and an elusive peak seen by the same experimenters in the elastic scattering of electrons from helium at 21.4 to 21.6 eV, just above the $n = 2$ levels. Schulz and Philbrick (1965) and Chamberlain and Heideman (1965) observed a stronger peak in the inelastic cross section of He corresponding to nearly the same energy. TNG attribute this resonance to a CE2 above the $n = 2$ level of He, rather than a CE1 below the $n = 3$ level, as the necessary binding energy below the $n = 3$ level would indicate a longer lived resonance and therefore a narrower peak than that observed, and an electron affinity of 2 eV for the $n = 3$ level as opposed to .1 to .6 for the $n = 2$ level.

In the same spirit, it is argued that if an excited target state can support virtual levels, it should be possible for the ground state to do so also. Several experimental observations exist which cannot be explained except by postulating such states, which TNG classified as Single Particle since the physical model assumed is the

nearly unperturbed ground state plus an orbiting planetary electron. These states are also expected to be quite broad.

The experiments leading to these conclusions are the N_2 - electron scattering experiments of Schulz (1962, 1964, 1966), the H_2 - electron dissociative attachment experiment of Schulz and Asundi (1966), and structure in the elastic He - electron scattering cross section at about 0.45 eV observed by Schulz (1965).

The introduction of the CE2 and SP resonances requires a more effective procedure for calculating the energy of resonances.

TNG, with the assistance of the author, presented a stabilization method which generalizes the quasi-stationary methods mentioned above (page 3), and incorporates a way of handling CE2 and SP as well as CE1 resonances.

The methods of calculating the resonant energies are basically refinement methods. The wave function of the resonant state is written as a superposition of configurations selected on the basis of experimental results and intuition. The refinement method is used to improve the wave function by calculating correction terms. Even though this method is an approximate method, it will be justified below on formal grounds. The most direct justification of the method, however, is the fact that it allows one to calculate ab-initio very good approximations to the experimentally observed resonant energies.

In order to gain perspective it is well to consider for the moment how one might calculate an approximate wave function and energy of an excited bound state of an atom or molecule. If the state in

question is the M th excited state of a given symmetry one might choose a large number of properly symmetrized basis functions (greater than M), diagonalize the Hamiltonian of the system and optimize the M th root according to the Hylleraas-Undheim procedure. However, if the state is very highly excited such a procedure will in general not give a good result. One is thus forced to try other methods. There are two possible alternative approaches: a variation-perturbation method or a quasi-variation technique. In a variation-perturbation method one chooses a zero-order wave function and then corrects it by variational versions of perturbation techniques. Such perturbation methods include the inverse nuclear charge method (Knight and Scherr, 1963), the method of Kirtmann and Decious (1966) and the methods of Hirschfelder et al. (1965) and Byers Brown et al. (1966). These methods are convenient to apply if the system is not too large. For larger systems one is forced to use quasi-variational approaches in which a limited number of configurations is selected on intuitive grounds. These configurations are then optimized variationally by means of linear and non-linear parameters. In such methods one must be careful that the final wave function does have dominant those configurations which one feels on intuitive grounds should be dominant. One adds other configurations to the wave function to see if the mixing is appreciable and constantly checks whether the energy is stabilized. In other words, in practice one must use intuition to a large degree to guide the variational method towards the desired result.

All of the methods mentioned above depend for their success on

the choice of trial functions. The Hylleraas-Undheim method will give poor results if the basis set is chosen poorly; the perturbation methods will give poor or entirely wrong results if the zero-order function is not chosen properly; the quasi-variation of linear and non-linear parameters will also give poor or incorrect results if the configurations chosen do not fit the physics. In the following discussion it will be shown that the situation is much the same in resonant-state calculations.

In order to discuss resonances let us consider a scattering experiment in which a projectile is scattered by a target. The target might be a nucleus and the projectile a neutron or proton as in nuclear physics, or the target might be an atom or molecule and the projectile an electron as in electron-impact spectroscopy. Let us consider an experiment in which a beam of projectiles is fired from a gun at the target, scattered by the target and then detected in a detector. The entrance channel is thus an incoming projectile with the target in the ground state. If the energy of the projectile is insufficient to excite the target, the scattering is elastic and the exit channel will be an outgoing projectile with the target in the ground state. Far from the scattering center (i.e. in the detector) the wave function for the total system is thus a product of the ground-state target wave function and a sum of incoming projectile waves and outgoing spherical projectile waves.

A traditional way of describing an elastic resonance in nuclear physics (Blatt and Weisskopf, 1952) is to say that at certain kinetic

energies the incoming projectile penetrates the target and forms a compound system. The compound system exists for a short time and then decays back into a target in the original state and an elastically scattered electron. The presence of the compound state is evidenced by a sharp and narrow resonance in the elastic scattering cross section at the so-called resonant energy. The possible resonant energies, i.e. the energies of the possible resonant states, are obtained by excluding the incoming and outgoing waves and solving for the energy levels of the compound projectile-target system as if it were a bound system.

One possible way of excluding the incoming and outgoing continuum contributions to the resonant wave function is to put the compound system in a box. In nuclear physics this is a reasonable procedure. The surface of the box would be the surface of the compound nucleus. Since nuclear forces are short-ranged, one can meaningfully define a nuclear surface and can partition physical space into inside the compound nucleus and outside the compound nucleus. However, in the case of electron-atom or electron-molecule scattering it is difficult to define a box because of the long-range Coulombic electron-electron forces. One achieves the effect of putting the compound system in a box by partitioning the Hilbert space of the compound-system Hamiltonian instead of physical space. The Hilbert space is partitioned into P -space which contains all functions expandable in terms of the asymptotic exit channels and into Q -space which contains all functions having no projection on the asymptotic exit channels. Hence, one

diagonalizes the compound-state Hamiltonian in Q -space. The solutions so obtained can have meaning only in the situation in which the electron is confined to the vicinity of the target. The electron has thus been put in a box whose radius is the range of the effective scattering potential without even specifying that radius. It will be shown formally below that diagonalizing the Hamiltonian in Q -space is equivalent to diagonalizing the pseudo-Hamiltonian $QHQ = H_{QQ}$ in the full Hilbert space. The operator Q is a projection operator which selects Q -space. The method of calculating resonances thus reduces to diagonalizing the compound-system projectile-target Hamiltonian with as large a basis set as is possible which does not include the asymptotic exit channels.

Let us consider the case of electron-atom scattering. The projectile is an electron and the target is an N -electron atom presumed to be in its ground state. The total energy of the system is the kinetic energy of the incoming electron and the ground-state energy of the atom. In order to obtain the resonant states (and energies) of the $(N + 1)$ -electron atom one looks for apparent bound states of the $(N + 1)$ -electron Hamiltonian in the vicinity of the experimental energy. Therefore, in order to calculate the resonant energies of the electron-atom system, one must diagonalize the full $(N + 1)$ -electron Hamiltonian of the total system as mentioned above.

The problem which is encountered is that as mentioned above the energy of the resonant state will not in general correspond to the lowest root of the $(N + 1)$ -electron Hamiltonian. The situation is

thus similar to that encountered in solving for the energy of a very highly excited bound state, hence one can use either perturbation-variation or quasi-variation methods to zero in on and stabilize the desired root. In order for a root-stabilization method to work the energy of the intuitively-guessed wave function must be close to the actual resonant energy. It is only in such a case that one can safely discard any configuration which seriously alters the energy. One expects a root-stabilization method to work because the electrons most involved in the resonances cannot be highly correlated. If they were highly correlated, the resonant state would not possess a long enough lifetime to be observed experimentally. The low correlation indicates that a one-electron picture (i.e., trial function as product of one electron orbitals, or small linear combination of products) is meaningful. One therefore expects the energy of the resonant state to have essentially settled down to its final value, i.e. to have become stabilized, after mixing a few configurations with the intuitively guessed one(s).

A word of caution is necessary on the use of a stabilization method. If a root cannot be stabilized with a small number of configurations either an incorrect wave function has been chosen to start with or the basis set is not a good one. If very closely-spaced roots begin to occur, then the concept of root-stabilization becomes meaningless and the method is inapplicable. This would be the case if the resonant state belonged to a group of very closely-spaced resonant states. The desired state would be a member of a group of almost

degenerate resonant states in this case. In such a case one would have to consider all of the almost degenerate resonant states as a unit.

The quasi-variation method of Taylor and Williams (1965) and the equivalent method of O'Malley and Geltman (1965) can now be seen to be incomplete. In these methods the Q -space was constructed by eliminating from the basis set all configurations containing those target states included in the exit channels, i.e. they eliminated all parent target states lying below the resonant state. Therefore, these methods could not be used to calculate single-particle or type II core-excited resonant states because they lie above their parent target states. These methods do give results for core-excited type I resonant states comparable with experiment since the core-excited resonant states do not involve to a large degree the lower lying parent target states. Because of the small correlation between the extra electron and the target, the ground target states do not mix very strongly. In other words, the quasi-variation method is a way of zeroing in on the root for those resonant states in which the wave function does not include appreciable overlap with the initial target states (i.e. those target states occurring in the exit channels). The Q -space of the quasi-variation method is a subspace of the more general Q -space of the stabilization method.

The obvious fault of the stabilization methods is that they do not calculate lifetimes. One could stabilize, especially in the case of a single-particle or type II core-excited resonant state, on a root corresponding to a resonant state which is too short-lived to be

observed experimentally. The perturbation method will definitely calculate such short-lived resonant states if the choice of zero-order wave function forces it to do so. In the case of type I core-excited resonant states we are confident that the lifetimes are of the order of 10^{-14} to 10^{-13} seconds. For single-particle of type II core-excited resonant states experience and intuition are not well enough developed to allow even rough estimates.

Now that the quasi-stationary methods have been described, it remains to show that the eigenfunctions and eigenvalues they yield do correspond to resonant states. In this section the Feshbach theory of resonant reactions (1958, 1962) will be used to establish this correspondence by showing that eigenfunctions of $QHQ = H_{QQ}$ do lead to a Breit-Wigner form in the cross section and correspond to a decaying bound state.

The equation to be solved is the $(N + 1)$ -electron Schrödinger equation for the projectile-target system

$$H\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{N+1}) = E\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{N+1}) \quad (1)$$

for a given energy E . The operator H is the full Hamiltonian of the system and $\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{N+1})$ is the total wave function. The procedure used by Feshbach (1962) is to partition space with two projection operators P and Q such that they satisfy the relationships

$$P\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{N+1}) \xrightarrow[1 \leq i \leq N+1]{r_i \rightarrow \infty} \Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{N+1}) \quad (2)$$

and

$$P + Q = 1$$

$$P^2 = P, Q^2 = Q \quad (3)$$

$$PQ = QP = 0$$

The projection operator P projects out of the wave function all components on the available asymptotic exit channels at the given energy E .

The Schrödinger equation, Eq. (1) can now be solved formally in a way which will show the resonances explicitly. Writing $\Psi = Q\Psi + P\Psi$ Feshbach partitioned Eq. (1) into a set of two coupled equations

$$(H_{PP} - E) P\Psi = -H_{PQ} Q\Psi \quad (4a)$$

and

$$(H_{QQ} - E) Q\Psi = -H_{QP} P\Psi \quad (4b)$$

where $H_{PP} = PHP$, etc. Solving Eq. (4b) for $Q\Psi$ and inserting the result into Eq. (4a) yields

$$\left(H_{PP} + H_{PQ} \frac{1}{E - H_{QQ}} H_{QP} \right) P\Psi = EP\Psi \quad (5a)$$

or

$$(H_{PP} + V_{opt}) P\Psi = EP\Psi \quad (5b)$$

where V_{opt} is the optical potential. In order explicitly to introduce the resonances into the picture one must consider the equation

$$(H_{QQ} - \epsilon_n) \phi_n = 0 \quad (6a)$$

If this equation has eigensolutions, they must be eigenfunctions of Q with eigenvalue unity, i.e., $Q\phi_n = \phi_n$, and Q can be expanded in terms of its eigenfunctions as

$$Q = \sum_n |\phi_n\rangle\langle\phi_n| \quad (6b)$$

where the summation includes the integral over the continuum if necessary. Inserting this expression into V_{opt} yields

$$\left(H_{\text{PP}} + \sum_n \frac{H_{\text{PQ}}|\phi_n\rangle\langle\phi_n|H_{\text{QP}}}{E - \epsilon_n} \right) \text{P}\Psi = E\text{P}\Psi \quad (7)$$

Therefore, the optical potential has poles at energies equal to the eigenvalues of Eq. (6). In the case of well-separated resonances one can break up the optical potential into two parts when E is near one of the ϵ_n , say ϵ_s . Thus, Eq. (7) may be rewritten as

$$\left(H_{\text{PP}} + \sum_{n \neq s} \frac{H_{\text{PQ}}|\phi_n\rangle\langle\phi_n|H_{\text{QP}}}{E - \epsilon_n} - E \right) \text{P}\Psi = - \left(\frac{H_{\text{PQ}}|\phi_s\rangle\langle\phi_s|H_{\text{QP}}}{E - \epsilon_s} \right) \text{P}\Psi \quad (8a)$$

or, by definition of H' ,

$$(H' - E)\text{P}\Psi = - \left(\frac{H_{\text{PQ}}|\phi_s\rangle\langle\phi_s|H_{\text{QP}}}{E - \epsilon_s} \right) \text{P}\Psi. \quad (8b)$$

The operator H' is that part of the Hamiltonian which varies slowly with the energy E and gives rise to non-resonant scattering while the operator $H_{\text{PQ}}|\phi_s\rangle\langle\phi_s|H_{\text{QP}}/E - \epsilon_s$ gives the rapidly changing, or resonant, contribution to the scattering.

The first step in solving Eq. (8b) is to solve the homogeneous portion $(H' - E)\text{P}\Psi_0^+ = 0$, where the $+$ indicates that the solution

satisfies outgoing boundary conditions and minus indicates that the solution satisfies incoming boundary conditions. The functions $\mathbf{P}\Psi_{\mathbf{O}}^{\dagger}$ describe non-resonant scattering since they are associated with H' . It is assumed that $\mathbf{P}\Psi_{\mathbf{O}}^{\dagger}$ exist and are known. Given the set of $\emptyset_n$ from Eq. (6) and $\mathbf{P}\Psi_{\mathbf{O}}^{\dagger}$ one can investigate the T matrix (see Goldberger and Watson, 1964) and thus the scattering cross section. From the outgoing homogeneous solution $\mathbf{P}\Psi_{\mathbf{O}}^{\dagger}$ a Green's function can be constructed and an integral equation for the total outgoing solution $\mathbf{P}\Psi^{\dagger}$ can be derived, namely

$$\mathbf{P}\Psi^{\dagger} = \mathbf{P}\Psi_{\mathbf{O}}^{\dagger} + \frac{1}{E^+ - H'} \frac{H_{\mathbf{PQ}} |\emptyset_S\rangle \langle \emptyset_S| H_{\mathbf{QP}} | \mathbf{P}\Psi^{\dagger} \rangle}{E - \epsilon_S} \quad (9)$$

Operating on the left with $\langle \emptyset_S | H_{\mathbf{QP}}$ on both sides of Eq. (9) one finds the relation between $\langle \emptyset_S | H_{\mathbf{QP}} | \mathbf{P}\Psi^{\dagger} \rangle$ and $\langle \emptyset_S | H_{\mathbf{QP}} | \mathbf{P}\Psi_{\mathbf{O}}^{\dagger} \rangle$ which, after substitution back into Eq. (9), allows one to write $\mathbf{P}\Psi^{\dagger}$ as

$$\mathbf{P}\Psi^{\dagger} = \mathbf{P}\Psi_{\mathbf{O}}^{\dagger} + \frac{1}{E^+ - H'} \frac{H_{\mathbf{PQ}} |\emptyset_S\rangle \langle \emptyset_S| H_{\mathbf{QP}} | \mathbf{P}\Psi_{\mathbf{O}}^{\dagger} \rangle}{E - (\epsilon_S + \Delta^{(s)}) + \frac{1}{2} i\Gamma^{(s)}} \quad (10)$$

where, using Feshbach's notation,

$$\Delta^{(s)} - \frac{1}{2} \Gamma^{(s)} = \langle \emptyset_S | H_{\mathbf{QP}} \frac{1}{E^+ - H'} H_{\mathbf{PQ}} | \emptyset_S \rangle \quad (11)$$

Since the inverse operator $1/E^+ - H'$ can be written as

$$\frac{1}{E^+ - H'} = \mathcal{P} \left(\frac{1}{E - H'} \right) - i\pi \delta(E - H') \quad (12)$$

the explicit definitions of the energy shift $\Delta^{(s)}$ and the level width $\Gamma^{(s)}$ are

$$\Delta^{(s)} = \langle \emptyset_S | H_{\mathbf{QP}} \mathcal{P} \left(\frac{1}{E - H'} \right) H_{\mathbf{PQ}} | \emptyset_S \rangle \quad (13)$$

and

$$\Gamma^{(s)} = 2\pi \langle \emptyset_S | H_{QP} \delta(E-H') H_{PQ} | \emptyset_S \rangle \quad (14a)$$

or, equivalently, using the expansion $H_{PQ} | \emptyset_S \rangle = \int a(E') | P\Psi_0^+(E') \rangle dE'$

$$\Gamma^{(s)} = 2\pi | \langle \emptyset_S | H_{QP} | P\Psi_0^+(E_S) \rangle |^2 \quad (14b)$$

The T matrix for the effective Schrödinger equation (8b) is

$$\langle \chi_0 | T | \chi_0 \rangle = \langle \chi_0 | V | P\Psi^+ \rangle \quad (15)$$

where χ_0 is the eigenfunction of that part of H' , called H_0 , which describes unperturbed motion of the incident particle and target system, that is H_{pp} , and where according to Eq. (8) V is given by

$$V = V_{\text{non-resonant potential}} + \left(\frac{H_{PQ} | \emptyset_S \rangle \langle \emptyset_S | H_{QP}}{E - \epsilon_s} \right)_{\text{resonant potential}} \quad (16)$$

Inserting $P\Psi^+$ from Eq. (10) into Eq. (15) and recalling that $P\Psi_0^+$ is the outgoing non-resonant scattering solution of $(H' - E)P\Psi_0^+ = 0$ and therefore satisfies

$$P\Psi_0^+ = \chi_0 + \frac{1}{E^\pm - H_0} (H' - H_0) P\Psi_0^+ = \left[1 + \frac{1}{E^\pm - H'} (H' - T_0) \right] \chi_0 \quad (17)$$

it is seen after some manipulation (see Goldberger and Watson, 1964, sec. 5.4)

$$\begin{aligned} \langle \chi_0 | T | \chi_0 \rangle &= \langle \chi_0 | H' - H_0 | P\Psi_0^+ \rangle_{\text{non-resonant}} \\ &+ \left(\frac{\langle P\Psi_0^- | H_{PQ} | \emptyset_S \rangle \langle \emptyset_S | H_{QP} | P\Psi_0^+ \rangle}{E - (\epsilon_s + \Delta^{(s)})} + \frac{1}{2} i\Gamma^{(s)} \right)_{\text{resonant}} \end{aligned} \quad (18)$$

Since the cross section is proportional to the square of the T matrix, it will show a Breit-Wigner form and will change rapidly at $E \approx \epsilon_s + \Delta^{(s)}$ with a half-width of $\Gamma^{(s)}$. When E is not near $\epsilon_s + \Delta^{(s)}$ the non-resonant term will dominate and the cross section will vary smoothly with the energy.

Thus with a rigorous formalism applicable to both atomic and molecular cases it has been shown that the eigenfunctions of the effective Hamiltonian H_{QQ} , Eq. (6), do indeed lead to rapid changes of the Breit-Wigner type in the scattering cross section when the energy E is near an eigenvalue of H_{QQ} . It is assumed that H_{QQ} does have bound-state solutions in the vicinity of the energy E . If this is not the case, the resonant term will obviously vanish at that energy.

In order to interpret what is happening physically when a resonance occurs it is necessary to form a wave packet centered about the energy E . To determine with good precision the time at which the particle enters the "internal region," where $Q\Psi$ is non-zero, a sharp wave packet involving a broad range of energies ΔE must be constructed with the assumption that $\Delta E \gg \Gamma$. Choosing $t = 0$ as the time at which the incident particle enters the internal region, the part of the packet due to the $Q\Psi^+$ part of Ψ^+ at $t = 0$ may be written as

$$Q\Psi(\underline{r}, t) = \int_{\Delta E} C(E) Q\Psi^+(E) e^{-iEt} dE \quad (19)$$

where $C(E)$ is a slowly varying function of energy. From the

expression

$$Q\Psi = \frac{1}{E^+ - H_{QQ}} H_{QP} P\Psi^+ \quad (20)$$

it can be shown that, for E near ϵ_s , one has

$$Q\Psi(\underline{r}) \approx \frac{\frac{1}{2} \sqrt{\frac{2}{\pi\Gamma(s)}} \Gamma(s)}{E - (\epsilon_s + \Delta(s)) + \frac{1}{2} i\Gamma(s)} \varnothing_s(\underline{r}) \quad (21)$$

To see this one has to introduce the operator Q (in Eq. (6b)) before the H_{QP} operator in Eq. (20) and the expression (10) for $P\Psi^+$, and select all resonant terms of the resulting expression which have the factor $1/E^+ - \epsilon_s$. In the final step one has to replace $\langle \varnothing_s | H_{QP} | P\Psi_O^+ \rangle$ by its absolute value (changing in this way only the phase factor of $\varnothing_s$) and to realize that according to Eq. (14b) $|\langle \varnothing_s | H_{QP} | \Psi_O^+ \rangle| = \sqrt{\Gamma(s)}/2\pi$. Therefore at $t = 0$, $E \approx \epsilon_s$

$$Q\Psi(\underline{r}, 0) \approx \int_{\Delta E} C(E) \frac{\frac{1}{2} \sqrt{\frac{2}{\pi\Gamma(s)}} \Gamma(s)}{(\epsilon_s + \Delta(s)) - E - \frac{1}{2} i\Gamma(s)} \varnothing_s(\underline{r}) dE. \quad (22)$$

At time t this internal wave function becomes (since $\Psi^+(E)$ are eigenfunctions of H)

$$Q\Psi(\underline{r}, t) \approx C(\epsilon_s + \Delta(s)) \varnothing_s(\underline{r}) \int_{\Delta E} \frac{\frac{1}{2} \sqrt{\frac{2}{\pi\Gamma(s)}} \Gamma(s) e^{[-iE/\hbar]t}}{(\epsilon_s + \Delta(s)) - E - \frac{1}{2} i\Gamma(s)} dE \quad (23)$$

the assumption being made that ΔE is broad compared to the resonance at $\epsilon_s + \Delta(s)$, but small compared with the distance between successive

resonances. With the usual approximations for sharply peaked integrands, the integration limits may be extended to $-\infty$ and $+\infty$ yielding

$$Q\Psi(\underline{r}, t) \approx \frac{1}{2} \sqrt{\frac{2}{\pi\Gamma(s)}} \hbar\Gamma(s) C(\epsilon_s + \Delta(s)) \phi_s(\underline{r}) \times \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{\left[(\epsilon_s + \Delta(s)) - \frac{1}{2} i\Gamma(s) \right] - \hbar\omega} \quad (24)$$

This familiar integral (in time-dependent perturbation theory) can be evaluated to give (see Goldberger and Watson, chapter 8)

$$Q\Psi(\underline{r}, t) = \begin{cases} \sqrt{\frac{2}{\pi\Gamma(s)}} \pi i\Gamma(s) C(\epsilon_s + \Delta(s)) \phi_s(\underline{r}) & t > 0 \\ \times e^{-i/\hbar(\epsilon_s + \Delta(s))t} e^{-\Gamma(s)/2\hbar t} & \\ 0 & t < 0 \end{cases} \quad (25)$$

The $Q\Psi$ part of the wave packet thus comes into effect as the particle comes into the region of the target. In this region the $Q\Psi$ part of the packet and thus the $N+1$ electron system resembles a stationary eigenfunction of H_{QQ} except for the fact that this "stationary" state is modulated and decreased in time by an exponential decay factor with mean lifetime $\tau = \hbar/\Gamma(s)$. It has therefore been shown that the $N+1$ particle system does exist as a quasi-stationary localized state for an average time τ . If one looks at Messiah's development of radiation theory, (1963) where projection operators are used to separate the light field from the matter states, one sees that the use of the word

"stationary" in describing the states of negative ions is either rigorous or approximate in the same sense that one calls "stationary" any excited state of an atom or molecule that has a finite spontaneous emission probability.

The beauty of the projection operator formalism is its generality. It does not depend on the choice of H , and Q and P are only required to satisfy $P\Psi \rightarrow \Psi$ at large distances, so that the formalism can be applied to any decaying state problem. Note, however, that both the formal theory and the quasi-stationary methods require that the physical situation be inserted, either by chemical intuition or by proper choice of the projection operators P and Q . This is the price which must be paid for not being able to integrate the Schrödinger equation exactly.

CHAPTER III

RESONANT STATES OF H_2^- *

Introduction

In this paper the quasivariation method developed simultaneously by Taylor and Williams (1965, hereinafter denoted by TW) and O'Malley and Geltman (1965), and the stabilization method discussed in the work of Taylor, Nazaroff, and Golebiewski (1966, hereinafter denoted by TNG) are applied to the ab initio calculation of quasi-stationary states of H_2^- . Results are compared quantitatively and qualitatively to dissociative attachment, vibrational excitation and electron scattering experiments.

For the definitions of, and distinctions between the three types of resonance calculated here (Single Particle and Core-Excited Types I and II, hereinafter denoted by SP, CE1, and CE2, respectively); the usefulness of these definitions and a discussion and derivation of the variational principles used in the present work, see the paper of TNG.

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Experiments and Results

The experiments simplest to explain with the calculations presented here are those in which resonances are seen in the total and inelastic electron-hydrogen cross section. Such observations have been made by Kuyatt, Simpson and Mielczarek (1964, 1965b, 1966) in transmission experiments, by Golden and Bandel (1965) with a modified Ramsauer technique and by Heidemann, Kuyatt, and Chamberlain (1966) in inelastic scattering experiments. These resonances are attributed to the formation of two short-lived states of H_2^- , and the individual peaks in the cross section correspond to definite vibrational levels of the resonant molecular state. The well-developed vibrational structure indicates a lifetime sufficiently long for molecular vibrations of the order of 10^{-13} sec.¹

As was noted in all publications on these resonances, there is a striking resemblance of the vibrational spacings of the two resonances themselves, and also of the spacings of the resonances and the spacings of the four H_2 states $c^3\Pi_u$, $a^3\Sigma_g$, $C^1\Pi_u$ and $E^1\Sigma_g$.

¹In the earliest of their publications, Kuyatt et al. report only one resonant state. They later refined the experiment to observe two close-lying states. In TW, a rough calculation was carried out which agreed with the one resonance observed at that time. The general results of TW are still valid but are superseded by the more detailed calculations and analysis of this work. In this work, comparisons will be made with the later experiments of Kuyatt et al., which differ somewhat in energy scale from those of Golden and Bandel. This is admittedly done because of better agreement of the calculations with the Kuyatt work.

This indicates, as discussed in TNG, that the observed resonances are CE1, an electron in the field of a mixture of the four H_2 states above. Based on physical arguments, TW correctly credited the first resonance to a $^2\Sigma_g^- \sigma_g 1s \pi_u 2p_{+1} \pi_u 2p'_{-1}$ configuration of H_2^- , i.e., an electron in the field of the $^3\Pi_u$ state.²

The possible configurations that result from addition of an excited orbital to the four H_2 states and could cause resonances are listed in Table 1. Non-autoionizing configurations are omitted. In the third section, the details of the mixing of those configurations with the same symmetry in both the quasivariation and stabilization methods are reported.³

²Since we are using open shell calculations, a prime is used to indicate an orbital of slightly larger average radius than the unprimed orbital. The orbital notation is the standard Mulliken LCAO notation and is used for simplicity of presentation. Any particular Mulliken orbital can be thought of as the dominant term in an expansion of the molecular orbitals, used in this paper and explained in a later section, upon a complete set of Mulliken orbitals.

³Only the two $\sigma_g 1s \pi_u 2p_{+1} \pi_u 2p'_{-1}$ resonances and a portion of curve D of Fig. 1 were calculated with the quasivariation method as well as the stabilization method. The latter was used for all other H_2^- states. The reason for this is the difficulty encountered in orthogonalization of the wavefunction of the resonance to the wavefunctions of the states of H_2 of lower energy whenever the main configuration(s) has two orbitals which are not of π type. This orthogonalization is a requirement of the quasivariation method, but is not required when the stabilization method is used. The difficult orthogonality requirement will probably mean that most future calculations will be done by the stabilization method. Added to this difficulty in the quasivariation method is the fact that CE2 and SP resonances can only be calculated by the stabilization method, as discussed in TNG.

TABLE 1

SOME POSSIBLE H_2^- RESONANT STATES

H_2^-	Parent H_2 States
${}^2\Sigma_g^- \sigma_g 1s \pi_u 2p_{+1} \pi_u n p_{-1}$	$c^3\Pi_u, c^1\Pi_u$
${}^2\Pi_u \sigma_g 1s \pi_u 2p_{+1} \sigma_g 2s$	$c^3\Pi_u, a^3\Sigma_g^+, c^1\Pi_u, E^1\Sigma_g^+$
${}^2\Sigma_g^+ \sigma_g 1s (\sigma_g 2s)^2$	$a^3\Sigma_g^+, E^1\Sigma_g^+$
${}^2\Delta_g \sigma_g 1s (\pi_u 2p)^2$	$c^3\Pi_u, c^1\Pi_u$

Fig. 1.--Potential curves for H_2^- resonances and some associated H_2 states.

A - $H_2^- \ 2\Sigma_g^+$ consisting of $C^1\Pi_u \cdot \pi_u 2p'$

B - $H_2^- \ 2\Sigma_g^+$ consisting of $c^3\Pi_u \cdot \pi_u 2p'$

C - $H_2^- \ 2\Sigma_g^+$ consisting of $B^1\Sigma_u^+ \cdot \sigma_u 1s'$

D - $H_2^- \ 2\Sigma_g^+$ consisting of $3\Sigma_u^+ \cdot \sigma_u 1s'$

E - $H_2^- \ 2\Sigma_u^+$ consisting of $X^1\Sigma_g^+ \cdot \sigma_u 1s$

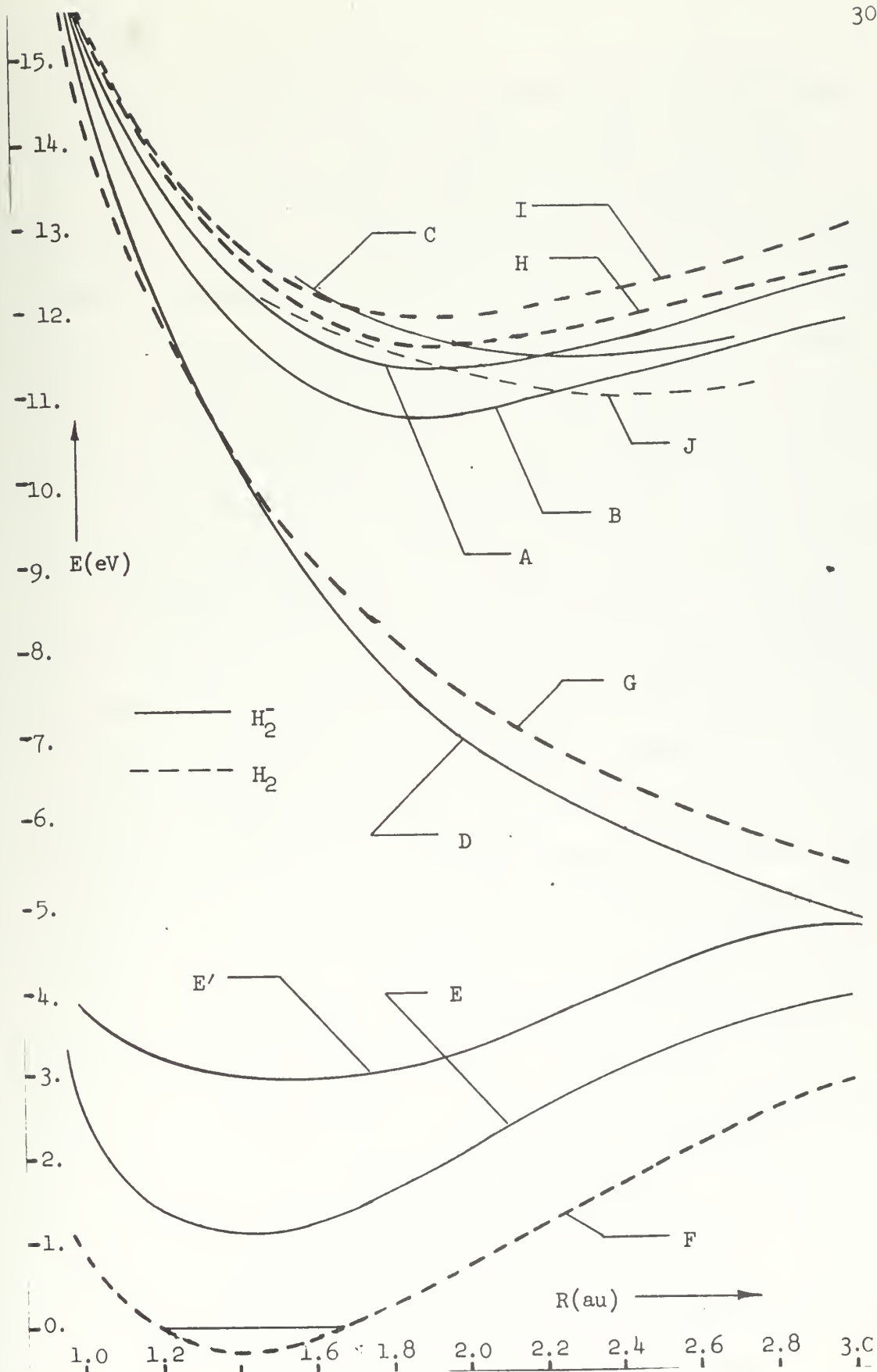
F - $H_2 \ X^1\Sigma_g^+$ (Kolos and Wolniewicz, 1965).

G - One configuration result for $H_2 \ 3\Sigma_u^+ \ 1\sigma_g 1\sigma_u$. This curve lies about 0.32 eV above the "exact" $3\Sigma_u^+$ curve (Kolos and Wolniewicz, 1965), but is used as a comparison with the H_2^- calculation consisting of this configuration plus an extra electron.

H - Two configuration result for $H_2 \ 3\Pi_u \ (1\sigma_g 1\pi_u + 1\sigma_u 1\pi_g)$. The minimum of this curve lies about 0.14 eV above the experimental minimum. The $H_2 \ a^3\Sigma_g^+$ curve lies so close to this one that they are indistinguishable on this scale.

I - Same as H for $C^1\Pi_u$ and $E^1\Sigma_g^+$

J - $H_2 \ B^1\Sigma_u^+$



The outstanding result of the present calculation for these two resonances was that the lower resonance is almost exclusively $^3\Pi_u + e$, $^2\Sigma_g^+ \sigma_g 1s \pi_u 2p_{+1} \pi_u 2p_{-1}'$ while the next resonance is $^1\Pi_u + e$, $^2\Sigma_g^+ \sigma_g 1s \pi_u 2p_{+1} \pi_u 2p_{-1}'$. In Table 2, the vibrational levels of these two states are compared to the observed levels of Kuyatt et al., and good agreement is obtained. The calculation also demonstrated a number of physical effects which were discussed in TNG. First, it was found that even though the two CE1 $\sigma_g 1s \pi_u 2p \pi_u 2p'$ states were mixed with themselves, with all the states of the same symmetry $^2\Sigma_g^+$ in Table 1, and with many configurations of non-stable H_2^- states of lower energy, the ratios of the off-diagonal elements of the Hamiltonian matrix to the diagonal elements were $\mathcal{O}(10^{-6})$ or less between the two spin doublets themselves, and between each of the spin doublets and the large number of other H_2^- configurations. This indicates the expected extremely weak interactions (low correlation) between electrons in the compound state. The electron affinity of the lower CE1 resonance is 0.8488 eV relative to its parent $^3\Pi_u$ state, and the higher CE1 resonance has 0.8435 eV binding relative to its $^1\Pi_u$ parent, or 0.276 eV relative to the $^3\Pi_u$.

CE1 resonances were not attainable from configurations representing an electron in the field of the other H_2 states in Table 1. No extensive search was made in this work for CE2 resonances belonging to the states of Table 1, although to check for their existence, one good stabilization calculation was done at the equilibrium internuclear separation of the four parent states ($R = 1.95$ au, $1 \text{ au} = .52917 \text{ \AA}$), for the configuration an electron in the field of $^3\Sigma_g^+; ^2\Sigma_g^+ \sigma_g 1s \sigma_g 2s \sigma_g 2s'$.

TABLE 2

COMPARISON OF EXPERIMENTAL
AND CALCULATED VIBRATIONAL LEVELS
(energies in eV)

Lower Resonance				Upper Resonance			
Obs. Level	Splitting	Calc. Level	Splitting	Obs. Level	Splitting	Calc. Level	Splitting
11.28		11.07		11.46		11.46	
	.28		.30		.26		.29
11.56		11.37		11.72		11.75	
	.28		.29		.27		.28
11.84		11.66		11.99		12.03	
	.27		.27		.28		.28
12.11		11.93		12.27		12.31	
	.26		.26		.26		.27
12.37		12.19		12.53		12.58	
	.25		.24		.24		.26
12.62		12.43		12.77		12.84	
	.24		.22		.20		.25
12.86		12.65		12.97		13.09	

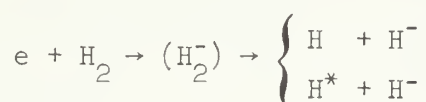
This root stabilized at an energy of -0.72911 au (1 au = 27.21 eV), 0.24 eV above $3\Pi_u$, $.3$ eV below $1\Pi_u$, $.13$ eV above $3\Sigma_g$, and 11.85 eV above the ground vibrational level of $H_2X^1\Sigma_g^+$, the reference zero level for all the calculated and experimental results. This root strongly indicates the existence of a CE2 resonance with this configuration which parallels its $3\Sigma_g^+$ parent with a slightly higher energy in the Franck-Condon region.

Again this $\sigma_g 1s \sigma_g 2s \sigma_g 2s'$ configuration does not mix with any of the $\sigma_g 1s \pi_u 2p \pi_u 2p'$ types and the resonance is expected to be quite broad relative to the CE1 resonances as discussed in TNG. It is likely that this resonance will only be observable in inelastic scattering experiments leading to its parent, however it is possible that threshold structure will obscure the observation. Because the two CE1 resonances are made from excited H_2 orbitals, it is to be expected that these resonant states are more strongly coupled to excited state exit channels of H_2 , and this accounts for the enhanced signal due to these resonances in elastic scattering (see Heidemann, Kuyatt, and Chamberlain, 1966).⁴

⁴In the next section, an even more tentative CE2 resonance, with the configuration of an electron in the field of $E^1\Sigma_g^+$, $2\Sigma_u^+ \sigma_g 1s \sigma_g 2s \sigma_u 2s$ is reported. The uncertainty of this resonance causes us to discuss it only in the next section, but it is mentioned here in the realization that many readers may not be interested in the detailed discussion of the calculations. Work is now in progress on this and other CE2 resonances expected to lie in this energy region. We emphasize that the two CE1 resonances and the single point at 11.85 eV are definitively stabilized and therefore represent final results.

In Fig. 2 the two CE1 resonances and the four aforementioned states of H_2 are shown, as well as the single point for the CE2 resonance (denoted by a cross). The solid lines represent the H_2^- CE1 resonances, the dashed lines the H_2 states, and the dotted line through the cross is the postulated potential curve of the CE2 resonance.

The next type of experiment to be discussed is dissociative attachment. The measured cross sections for the formation of the H^- ion in the process



are given in Figs. 3 and 4. In an as yet unpublished private communication, Dowell and Sharp have reported finding additional structure in the 8-12 eV peak. Besides the general Gaussian shape and the dip in the cross section at 11.2 eV, they have found a new series of dips on the high energy side of the peak, which have the feature of being spaced analogously to the spacings of the vibrational levels Kuyatt et al. found in their lower CE1 resonance. In TNG, it was shown how these experiments could be used to completely and definitively predict the position of the resonance potential curve causing such structural features as contained in the 8-12 eV peak. First, the general Gaussian shape, kinetic energy analysis, and isotope effect could be caused, as a result of Franck-Condon factors, by any repulsive resonant state with a potential curve which enters the Franck-Condon region of the ground vibrational level of the H_2 ground state at about 8 eV on the right, leaves it at about 13 eV on the left, and goes to the known

Fig. 2.--Comparison of the upper core-excited resonances to

H_2 .

$$A - H_2 \ c^3\Pi_u$$

$$B - H_2 \ C^1\Pi_u \text{ and } E^1\Sigma_g^+$$

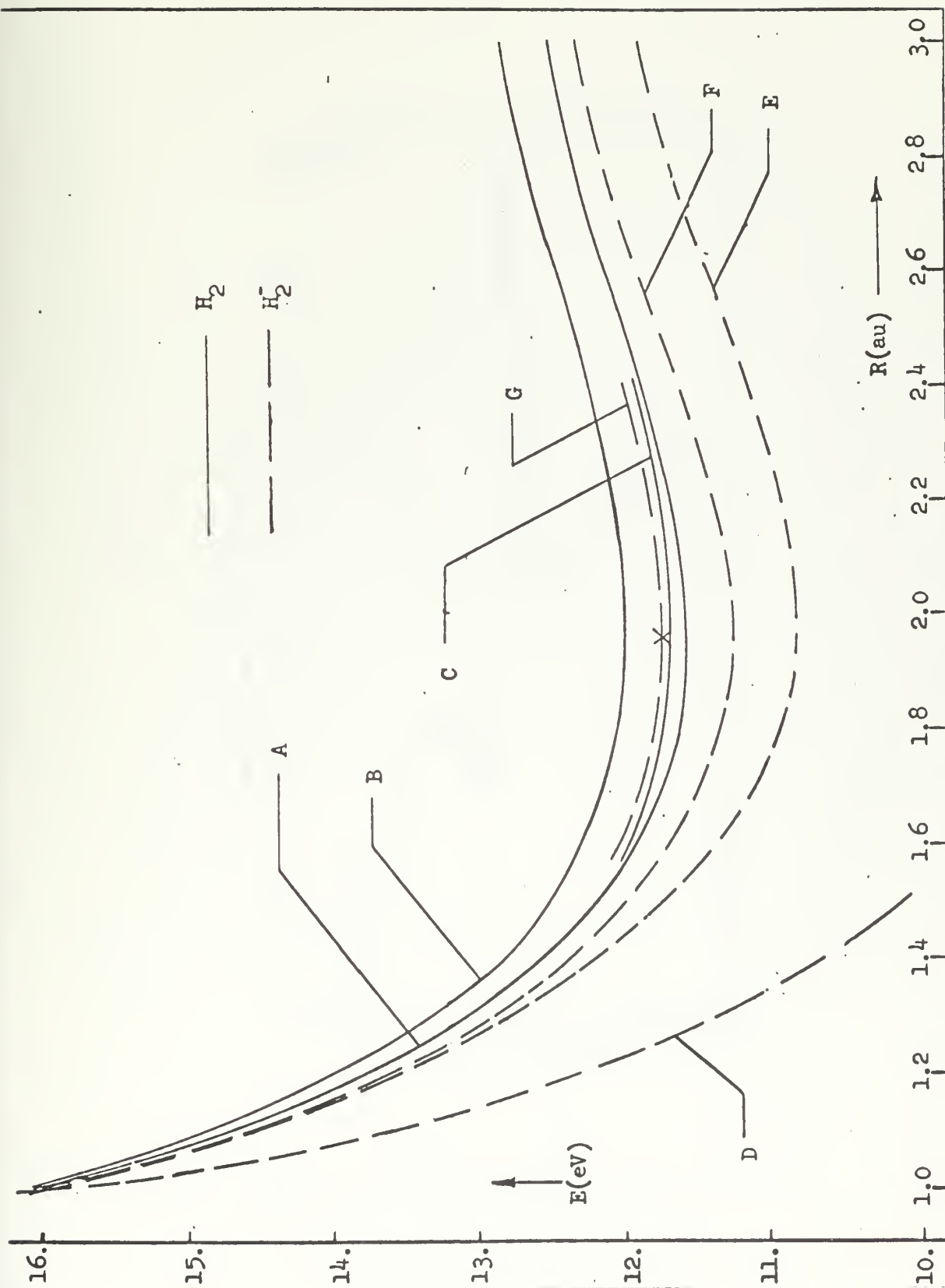
$$C - H_2 \ a^3\Sigma_g^+$$

$$D - H_2^- \ ^2\Sigma_g^+ \ \sigma_g 1s \sigma_u 1s \sigma_u 1s'$$

$$E - H_2^- \ ^2\Sigma_g^+ \ \sigma_g 1s \pi_u 2p \pi_u 2p' \quad ({}^3\Pi_u + \text{electron})$$

$$F - H_2^- \ ^2\Sigma_g^+ \ \sigma_g 1s \pi_u 2p \pi_u 2p' \quad ({}^1\Pi_u + \text{electron})$$

$$G - H_2^- \ ^2\Sigma_g^+ \ \sigma_g 1s \sigma_g 2s \sigma_g 2s' \quad ({}^3\Sigma_g^+ + \text{electron})$$



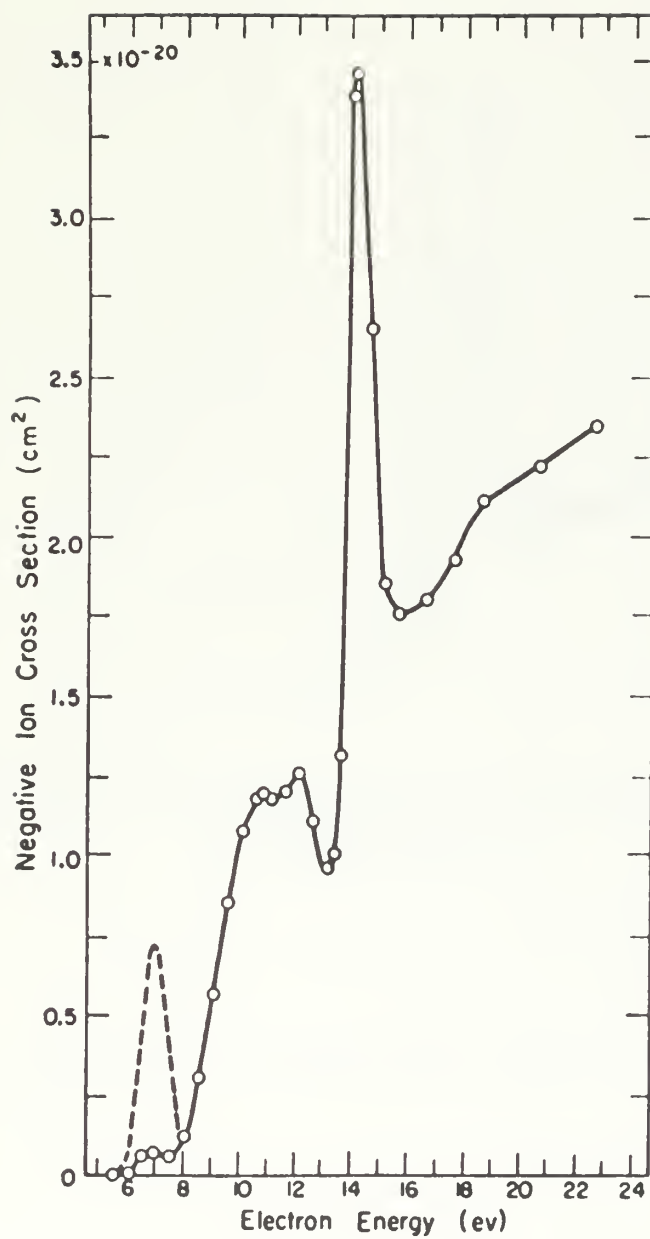


Fig. 3.--The dissociative attachment cross section of Scholz (1964).

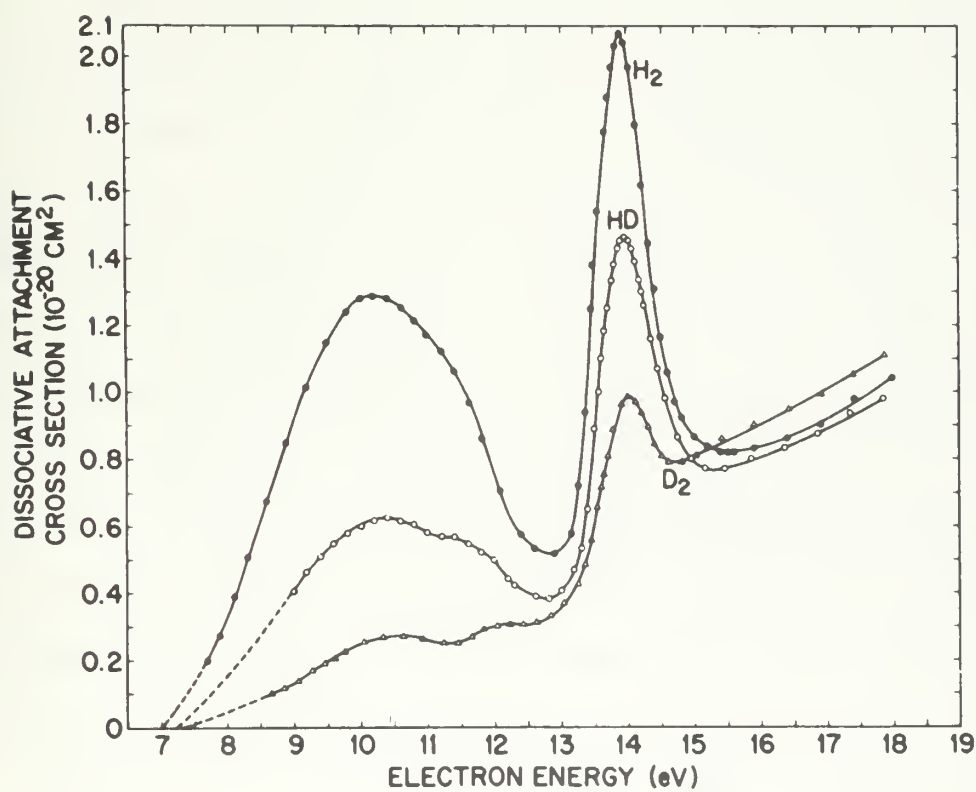


Fig. 4.--The dissociative attachment cross section of Rapp, Sharp, and Briglia (1965).

stable separated atoms H and H^- at an energy of 3.75 eV. The dip at 11.2 eV was most easily explained by assuming that this repulsive resonance potential curve could cross the repulsive $H_2^+ 3\Sigma_u^+$ state at 11.2 eV,⁵ thereby changing from a CE1 to a CE2 resonance, and opening a new exit channel $H + H + e$ to the system. Since, from the work of Kolos and Wolniewicz (1965), it is known that the $H_2^+ 3\Sigma_u^+$ state has a relative energy of 11.2 eV at $R \sim 1.29$ au, it can be concluded that the H_2^- has the same energy at this R .⁵ The opening of the new exit channel causes more of the H_2^- resonances formed at this energy to decay in channels other than that measured by dissociative attachment, and therefore causes a decrease in the cross section exactly at 11.2 eV. The reason that the cross section recovers its Gaussian envelope is illustrated in Fig. 5, where it is seen that only at the crossing point are the Franck-Condon factors of sufficient magnitude to make possible curve jumping to the $3\Sigma_u^+ + e$ channel.

The Dowell and Sharp result could most simply be explained by assuming that the resonance curve proceeds upward in energy until it approaches the lower $2\Sigma_g^+ \sigma_{1s} \pi_u 2p \pi_u 2p'$ CE1 resonance of Kuyatt et al. tangentially from the left. As shown in Fig. 6, if this were to occur, since both states are $2\Sigma_g^+$, one could get an inverse pre-dissociation from the repulsive H_2^- state to the bound H_2^- state at energies equal to

⁵Actually, in order to have the maxima of the nuclear wave functions coincide, the crossing would occur at a slightly lower energy, as shown in Fig. 5. As a consequence, the R value for the crossing point predicted by the dip will be slightly smaller than the actual R value at crossing.

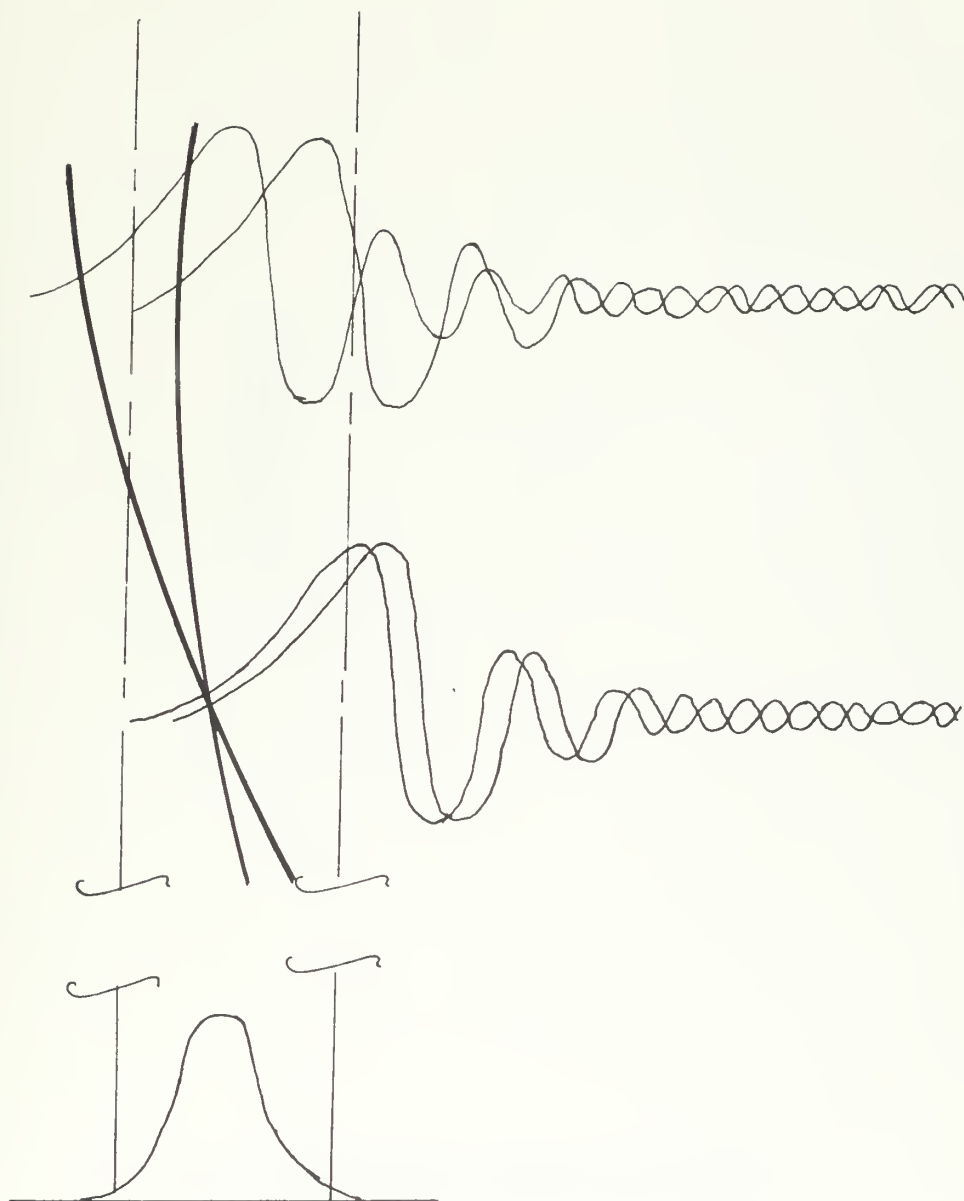


Fig. 5.--Comparison of Franck-Condon Factors.

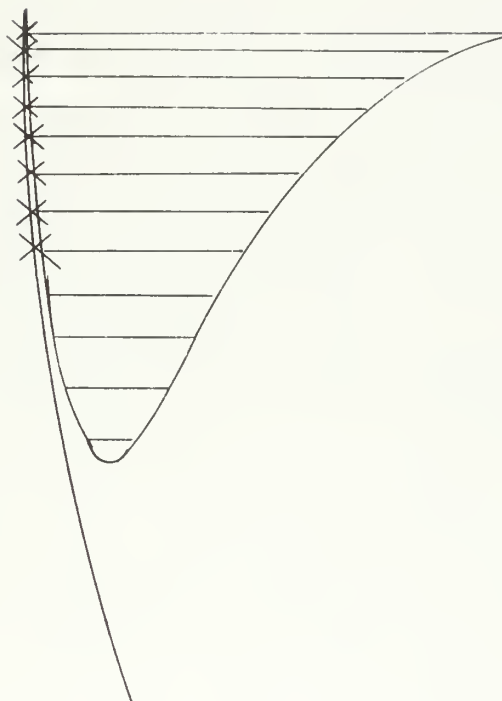


Fig. 6.--Schematic diagram for inverse pre-dissociation between resonances.

the vibrational levels of the upper resonance. Because of Franck-Condon factors (see Fig. 6) the postulated inverse pre-dissociation could only occur at vibrational levels of the upper resonance, and this could cause exactly the dips in the H^- formation cross section observed by Dowell and Sharp.

Since from experiment one knows the vibrational constants of the Kuyatt state, its potential curve can be determined empirically and the vibrational levels drawn in. By noting the energies and positions at which the vibrational levels and the empirical potential curve intersect, and by ignoring those points which do not correspond to dips in the Dowell and Sharp experiment, one is left with a set of points (denoted by crosses in Fig. 6) through which the repulsive resonance potential curve must pass. If one now smoothly connects the "cross" points of Fig. 6; the point on the $H_2 \ 3\Sigma_u^+$ curve; the point at which the 8 eV constant energy line intersects the large R, vertical Franck-Condon line; and the point at infinite R for the known $H + H^-$ energy, a curve (such as curve D of Fig. 1) is obtained with little ambiguity. In TNG, a conglomeration of tentative calculational, group theoretical, curve crossing and physical arguments were given to predict the curve, which, it was then pointed out, could explain the experiments. The opposite point of view is now being stressed, that once the type of phenomena that can occur in quasi-stationary molecular resonances are understood, and these are quite closely analogous to normal spectroscopic phenomena (i.e., dissociation, inverse pre-dissociation, pre-dissociation, etc.), one can predict where the resonant

TABLE 3

POTENTIAL CURVES OF H_2^- RESONANCES

R(au)	E(eV) ^g					
	a	b	c	d	e	f
1.05	2.15/3.72	14.4560	--	15.0315	15.0777	--
1.1	--	13.6693	--		--	--
1.2	1.41/3.22	12.5762	--	13.5654	13.6108	(17.15)
1.3	--	11.6103	--	12.8656	12.9403	(16.15)
1.4	1.22/3.04	10.6805	--	12.3197	12.4764	(15.88)
1.5	--	9.9254	12.742	11.8956	12.0941	--
1.65	1.37/3.03	9.0085	--	11.1802	11.6621	(14.49)
1.8	--	7.9560	11.896	11.0513	11.5439	(14.14)
1.95	--	7.0404	11.735	10.9090	11.4084	
2.1	--	6.9013	--	11.0405	11.4489	
2.25	--	6.3362	11.651	11.1115	11.6084	
2.4	--	5.8157	11.577	11.3615	11.8119	
2.7	--	5.4015	11.901	11.6609	12.1744	
3.0	3.87/4.90	4.8494	--	11.9949	12.4990	
				14.12	14.12	(13.92?)

$$a - {}^2\Sigma_u^+ \left(X^1\Sigma_g^+ + e, \sigma_g \sigma_g' \sigma_u \right)$$

$$b - {}^2\Sigma_g^+ \left(3\Sigma_u^+ + e, \sigma_g \sigma_u \sigma_u' \right)$$

$$c - {}^2\Sigma_g^+ \left(B^1\Sigma_u^+ + e, \sigma_g \sigma_u \sigma_u' \right)$$

$$d - {}^2\Sigma_g^+ \left(c^3\Pi_u + e, \sigma_g \pi_u \pi_u' \right)$$

$$e - {}^2\Sigma_g^+ \left(C^1\Pi_u + e, \sigma_g \pi_u \pi_u' \right)$$

$$f - {}^2\Sigma_u^+ \left(E^1\Sigma_g^+ + e?, \sigma_g \sigma_g' \sigma_u \right)$$

g - energies relative to ground vibrational level of H_2 $X^1\Sigma_g$

resonance in electron impact experiments where the cross section for excitation from the ground vibrational level of H_2 to excited vibrational levels is measured. Since the resonance potential curve does cross and go above the $3\Sigma_u^+$ channel in the Franck-Condon region, and thus lies very close to the H_2 state in the center of the Franck-Condon region, it is unlikely in any case that transitions through this resonance would make significant contributions to the vibrational excitation cross section to the lower H_2 vibrational levels.

The shape, isotope effect, and kinetic energy analysis of the 14.2 eV peak were explained in detail in TNG, and credited to transition to the dissociation limit of the two CEI $2\Sigma_g^+ 1s\pi_u 2p\pi_u 2p'$ resonances discussed above. The calculations presented here reinforce and are in complete agreement with the TNG arguments hence the arguments will not be repeated here. In a future paper, the wavefunctions calculated for these states as a function of internuclear distance will also be used in conjunction with the formal theories of dissociative attachment mentioned above.

It was postulated in TNG that the vibrational excitation results of Schulz (1964) and the dissociative attachment cross section, kinetic energy distribution, and sudden onset for the peak occurring at 3.75 eV (Schulz and Asundi, 1966) could be explained by the existence of what must be a quite broad SP resonance with the configuration $2\Sigma_u \sigma_g 1s \sigma_g 1s' \sigma_u 1s$, a $\sigma_u 1s$ electron in the field of $H_2 X^1\Sigma_g^+.$ ⁶

⁶The reader is referred to TNG for a discussion of why this configuration was chosen; why it is expected to be broad; why the resonance is difficult to observe in transmission, modified Ramsauer, and

The stabilization method has been applied for this state. A good ground state H_2 function was chosen, i.e., a three configuration, well correlated function which gave an energy at the minimum of the potential curve of -31.76 eV as compared to the experimental energy of -31.975 eV. The three configurations used were $\sigma_g ls \sigma_g ls'$; $\sigma_u^c ls \sigma_u^c ls'$; and $\pi_u^c 2p_{+1} \pi_u^c 2p'_{-1}$. The first configuration gives the main contribution around equilibrium nuclear separation R_e . The second is an axially correlating configuration near R_e and ensures proper breakup into two H atoms as $R \rightarrow \infty$, where it becomes as important as the $\sigma_g ls \sigma_g ls'$ configuration. The $\pi_u^c 2p \pi_u^c 2p'$ is an angular correlation configuration. The superscript c is added to these orbitals to indicate that they have the same average radial extent as the $\sigma_g ls$ orbital, and are specially optimized to produce the best H_2 ground state, as opposed to the $\sigma_u ls$ and $\pi_u 2p$ orbitals of the previous discussion which are similar to large excited orbitals of H_2 .

For the ${}^2\Sigma_u^- H_2^-$ calculation a third electron $\sigma_u ls$ was added to these configurations to give three three-electron configurations of symmetry ${}^2\Sigma_u^+$. This was then stabilized as discussed in the next section and resulted in the curve E of Fig. 1, as shown in detail in Fig. 7 and tabulated in Table 3. It is notable that even though one needs at least three configurations to represent this resonance well it is only because one must represent the target H_2 state to a high degree of accuracy. This type of configuration mixing does not

⁶total cross section experiments; and the general physics of the situation.

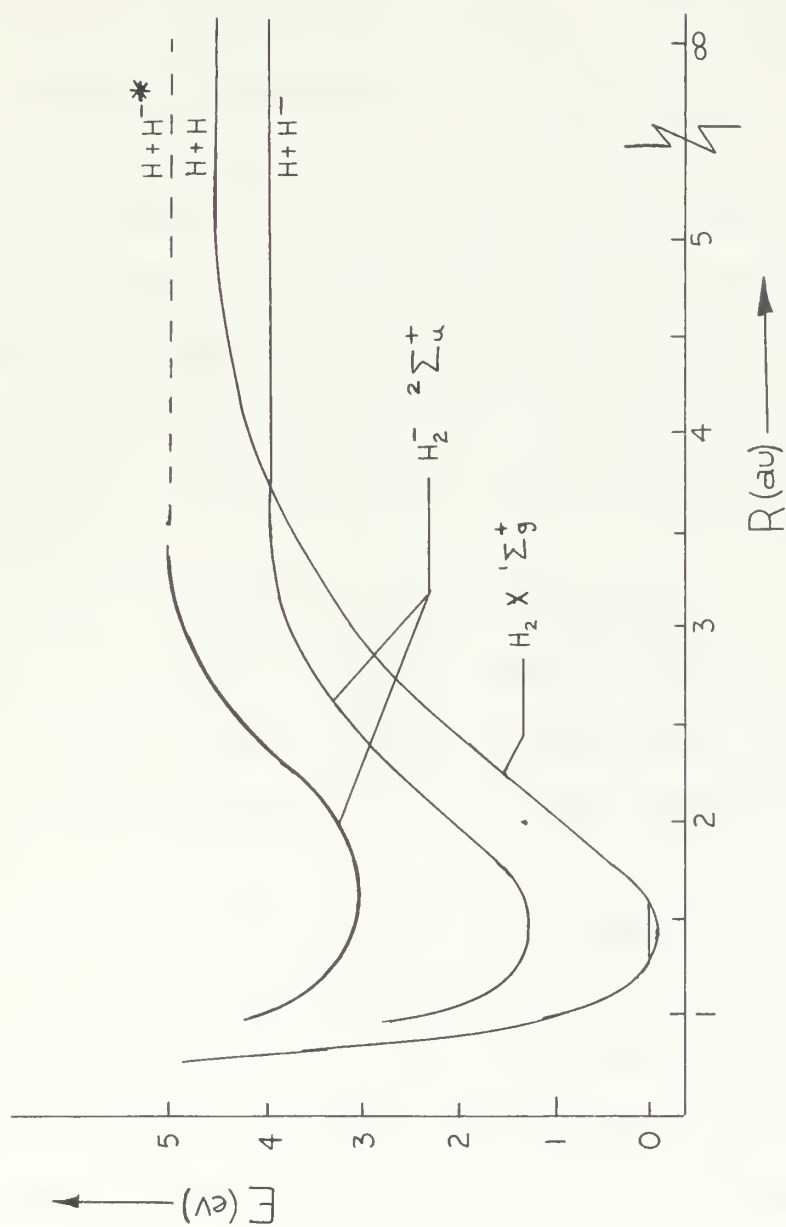


Fig. 7.--The single particle $H_2^- 2\Sigma_u^+$ states.

indicate strong correlation between the new electron and the original H_2 electrons. On the other hand, it was found that some configuration mixing was necessary before the root stabilized. This situation is analogous to that of the CE2 portion of the $^2\Sigma_g^- 1s\sigma_u 1s\sigma_u 1s'$ repulsive resonance, and again the extra mixing with the stabilizing configurations indicates that this resonance is quite broad. In any case, one finds a wavefunction with a small number of configurations whose eigenvalue was unaffected by further variations of the wavefunction. How much of this configuration interaction is due to width, and how much is due to a limited orbital functional form is impossible to tell.

The interesting features of this resonance are:

i) That at large R it connects smoothly to the $H + H^-$ $^2\Sigma_u^+$ state calculated by Taylor and Harris (1963) using a true variation method since at large R $H + H^-$ is the bound, lowest state of $^2\Sigma_u^+$ symmetry.

ii) That the potential curve for this state, once inside the curve for $H_2 X \ ^1\Sigma_g^+$, essentially parallels the H_2 curve from above, and turns up sharply at $R \sim 1.0$ au. Since its shape is like that of H_2 its harmonic vibrational constant will be similar to H_2 , and thus the lower vibrational levels will be at ~ 1.5 and 2.0 eV above the ground vibrational level of $H_2 X \ ^1\Sigma_g^+$.

The calculated state could well account for the dissociative attachment result of Schulz and Asundi (1966), but it should be pointed out that the dissociative attachment experiment in this case

gives no information about the position of the potential curve for the resonance inside the target H_2 potential curve.

From the vibrational excitation experiment, Schulz (1964) postulated the existence of a very broad resonance about 2.3 eV above the ground level of $H_2 \times 1\Sigma_g^+$. The result presented here is certainly lower than this. The only significant test of the calculated state that could be carried out, but for physical reasons, one which might not be extremely sensitive to the detailed form of the wavefunction, is to put the wavefunction calculated here into the formulae for the vibrational excitation cross section as presented by Bardsley, Herzenberg, and Mandl (1966a,b). This has been done by the latter authors using a wavefunction of significantly poorer quality than the one presented here⁷ and nevertheless resulted in a calculated cross section which is in quite acceptable agreement with the observed one.

⁷To demonstrate this point, one need only note that the Herzenberg et al. wavefunction gives rise to an H_2 energy of -30.44 eV and an equilibrium internuclear separation of 1.68 au. The wavefunction used in this work, gives an energy of -31.76 eV and an equilibrium separation of 1.4 au. The "experimental" values are -31.975 eV at 1.4011 au (Kolos and Wolniewicz, 1965). Because of the different qualities of the wavefunction and the wide variations in R_e , it is meaningless to try to compare the results of the present H_2^+ SP calculation with that of Herzenberg et al. Although one does not have a variation principle which says the lower the energy the better the function in these calculations, it is reasonable to assume that the more extensive and better functions used here will lead to more reliable results. The agreement with experiment in the Kuyatt et al. resonances, and the ability to explain the fine structure due to the repulsive resonance, which is completely lacking in the Herzenberg et al. results, seem to substantiate these claims.

In this laboratory the Herzenberg et al. calculations for the vibrational excitation cross section are being repeated with improved wave functions to see how sensitive the calculation is to the quality of the function.

The qualitative comparison of this state to the energy of Schulz is quite difficult since the SP state is so broad. In fact, in the vibrational excitation experiments, since the resonance is so broad, the nuclei do not have time to make definitive molecular vibrations, and Schulz was not able to distinguish any meaningful energies to determine the empirical potential curve for this state.

When the $^2\Sigma_u^+ (H_2 \times ^1\Sigma_g^-) \sigma_u$ 1s root was being stabilized, it was noted that a second root stabilized equally as well. The curve for this is E' in Fig. 1, and the upper H_2^- curve of Fig. 7. It seems to dissociate to $H + H^{-*}$ where H^{-*} is probably the very broad H^- resonance 1s 2s calculated by Herzenberg and Mandl (1963) to have an energy between 2.0 and 4.0 eV and a width of about 2 eV. This H_2^- state, again, will be very broad, and cannot be seen in a dissociative attachment experiment since a long-lived negative ion is necessary. As discussed in TNG, because of its breadth it also might be extremely difficult to detect in the total scattering cross section. Since it occurs at about 3 eV it could possibly contribute to vibrational excitation. One might speculate that both the 1.2 eV and 3.0 eV SP resonances contribute to give the broad vibrational excitation peak estimated by Schulz to be centered at 2.3 eV. Nothing definitive can be until calculations of widths and the vibrational excitation cross section have been made.

An interesting effect observed in these SP calculations was that the extra electron of the higher stable root had a smaller effective orbital radius than that of the lower root at small R ($\sim R_e$), but at large R the situation became reversed.

When stabilizing the repulsive $^2\sum_g \sigma_g 1s \sigma_u 1s \sigma_u 1s'$ state, in the calculations reported here, because of the open shell methods in which two spin doublets are used, a configuration $^2\sum_g \sigma_g 1s \sigma_u 1s \sigma_u 1s'$ (electron in the field of $B^1\Sigma_u^+$) was automatically included. During the stabilization process, a second root corresponding to this configuration also stabilized, and it was clearly a broad, CE2 resonance. This resonance, as in the other CE1 and CE2 cases, was well stabilized and highly uncorrelated and fits the rules given in TW and TNG for a resonance in the field of the B state. It should be difficult to observe for a number of reasons. As discussed in TNG, the breadth of this resonance favors its being looked for in inelastic experiments to vibrational levels of its parent B state. However, besides its breadth, the large R_e of ~ 2.45 au and the small ω_e of ~ 0.13 eV indicate that the resonance potential curve will be in such a position relative to the potential curve of the H_2 ground state that Franck-Condon factors will allow transitions only to the highly excited vibrational levels of the resonance ($v \sim 14$) and any structure may be obscured by the closeness of the spacings. It is impossible to tell from the published curves of Heideman, et al. (1966) whether there is any structure just above the excitation threshold, and since the width is not known, it is impossible to really argue whether or not such structure should indeed be observable.

The stabilization of this root, which fits the CE model of TW and TNG, brings up a very interesting and unanswered question; it seems that in the case of core-excited resonances a well stabilized root appears fastest whenever a configuration is used which puts the extra electron into the same type of orbital as the excited H_2 orbital [e.g., $\sigma_g(\sigma_u)^2$ and $\sigma_g(\pi_u)^2$]. Other configurations do not stabilize rapidly. Why this is so, we do not know, and it is freely admitted that the extent of calculational experience so far is not sufficient to say definitely that these other configurations do not stabilize, but there are strong indications that this is the case. Another strange effect arises when one adds many configurations solely for the purpose of testing the stability of a particular root. If the root under investigation is one which is truly stable, two or three stabilizing configurations are usually sufficient. On the other hand, other roots of the secular equation do eventually become constant after large numbers of configurations have been added, simply because the configurations made of orbitals which can mix with the configurations corresponding to these roots have been exhausted. A subject of future research, especially when reliable widths can be produced, will be a study of the significance of these more slowly stabilizing states. The authors stress that the states reported in the present work stabilized rapidly, and the confusion exists only about other less stable roots which were noted in the calculations.

In the tables and graphs the energies are reported in electron volts relative to the experimental ground vibrational level of H_2 in the ground state. When energies of resonances relative to energies of

H_2 are reported, the H_2 energies are those obtained with the same wave function as for H_2^- with the exception that the linear coefficients are re-optimized and the third electron is allowed to go to infinity. This is the only way to get a true comparison and does not yield misleading results since the wavefunctions used in the H_2 case give well over 99% of the total energy and an appreciable fraction of the correlation energy. In view of the experimental errors reported, improving the calculation of resonance and target energies to a degree of sophistication comparable to that of Kolos and Wolniewicz (1965), would do little to improve our understanding of the basic physics, and therefore would not justify the many man-hours and computer expenses involved.

A point of great interest arises when discussing the non-crossing rule of quantum chemistry. As noted by Bardsley et al. (1966), and the present authors, many unstable potential curves cross the stable potential curves. This would seem inadmissible by group theoretical arguments which say that the correct potential curves must be drawn by connecting the n^{th} lowest root at all R . These arguments have meaning in the variation method, but not, however, in the quasi-stationary methods used here. Bardsley et al. show this by reference to the work of Mandl (1966) in which it was proven that for resonant states calculated by the quasi-stationary complex energy Siegert method, the real part of the energy can cross (and this is what is calculated here) but that there is no crossing in the complex plane. While the authors have no argument with this correct interpretation, we prefer to present a more physically based model. To be specific, consider the

$2\Sigma_g^+ \sigma_{1s} \sigma_u \sigma_u \sigma_{1s}'$ repulsive resonant state, which at large R dissociates to H and H^- . This separated atom pair in turn lie about 1.0 eV below a pair H and H^{-*} , where the H^{-*} represents a SP resonance of H^- discussed by Herzenberg et al. The upper pair also has the symmetry

$2\Sigma_g^+$, but is $\sigma_{1s} \sigma_g \sigma_{1s}' \sigma_g 2s$.

In the united atom limit, the $2\Sigma_g^+ \sigma_{1s} \sigma_u \sigma_u \sigma_{1s}'$ state goes to an obviously core excited state of He^- , while the H and H^{-*} pair goes to $He^- 2S(1s)^2 2s$. The latter is clearly a very broad SP state of He^- and lies significantly lower than the core-excited state (about 19 eV). This means that the rapidly stabilizing $\sigma_{1s} \sigma_u \sigma_u \sigma_{1s}'$ root and the unstable $\sigma_{1s} \sigma_g \sigma_{1s}' \sigma_g 2s$ root, which are mixed to test the stabilization of the former, should cross at a reasonably large internuclear distance. This is exactly what was observed in the calculation. The solution to this dilemma is to realize that curve crossing is a dynamical as well as a group theoretical problem, and that the nuclear motion will thus follow the diabatic curve (wave function envelope) as opposed to the adiabatic curve (energy envelope) whenever the velocity of the nuclei is significant and the electronic interactions between the two wave-functions corresponding to the crossing curves is insignificant. In the case of core-excited resonances, it has already been pointed out several times that the mixing between the stable and added stabilizing configurations is 5-10 orders of magnitude smaller than the diagonal energy elements. (As discussed in TNG this fact is physically obvious and fundamentally the reason for the success of the quasi-stationary methods.) This means that in the problems considered here, the

diabatic curves are the ones which must be compared to experiment. The general procedure, therefore, is to follow the diabatic curves which can easily be chosen by studying the smooth change of wavefunction as a function of R , and then by looking to see if there is any significant mixing when two diabatic curves cross. A note of caution is in order — in processes like dissociative recombination and associative ionization, which are basically resonance processes, but where the relative kinetic energy of the nuclei is never more than $\sim .03$ eV at 300°K , one should follow the adiabatic curves. (A simplification is introduced in these problems, since the SP states are no longer resonances, but singly excited states of the system formed when an electron is added to the positive molecular ion, and therefore amenable to the quasivariation or variation methods.) In borderline cases, one will have to either refer to the theory of curve crossing, use Mandl's complex energy theorems, or hopefully, resolve the question unambiguously by comparison to experiment (one of the choices, diabatic or adiabatic, should give conspicuously poor agreement).

In this section any discussion of widths has been knowingly omitted. For the ${}^2\Sigma_g^+ \sigma_{1s} \sigma_{h1s'} \sigma_u \sigma_{1s}$ SP and ${}^2\Sigma_g^+ \sigma_{1s} \sigma_u \sigma_{1s} \sigma_{1s'}$ repulsive state, the widths have been calculated by Herzenberg et al., but for reasons that will be discussed in a future publication, the authors

reserve judgment as to their validity.⁸

It is clear for CE1 resonances that narrowness of width greatly favors the simplification introduced by using quasi-stationary methods, as opposed to pure close-coupled scattering calculations, when one only wishes to have information about the resonances' energy, width, and assignments. For CE2 and SP, which are quite broad [lifetimes of $O(10^{-14})$ sec or less]⁹ some authors would prefer to treat the phenomena associated with these states by pure scattering methods, especially the method of distorted waves. Herzenberg et al., in their calculation of the vibrational excitation cross section, stress that they obtain results with quasi-stationary methods for SP resonances¹⁰ which are in as good agreement with experiment as the result of Takayanagi (1965) which was achieved with a distorted wave method.

⁸The widths of resonances as calculated by complex energy methods similar to those used by Herzenberg et al. will be discussed in a publication in preparation by H. Taylor and A. Golebiewski. It will be shown there that the calculation of widths gives ambiguous results when the boundary enclosure (see Herzenberg et al.) is varied unless extremely large basis sets are used in the inside region. No calculations have ever been done using the complex energy method for widths in which extensive basis sets were used. Such calculations are in progress at this laboratory, and will be the subject of future communications.

⁹Single Particle resonances are expected to be even broader because of the relatively lower polarizability of the ground state.

¹⁰Various authors use the following names for what are denoted here by CE2 and SP: Shape resonances, virtual resonances, potential resonances, direct resonances, etc.

As pointed out by Herzenberg et al., this indicates that the two alternate models approach the true situation, that of a distorted target and an interacting passing electron, from two different limiting points of view.

The resonance formulation envisions a quasi-stationary state which must be coupled with outgoing waves, while the distorted wave method envisions a polarized target and a distorted orbit for the passing electron. Both of these approximations, if refined, will of course give the same result.

One can certainly say that the resonance formulation allows one to carry over the chemical concepts that are well known in spectroscopy and quantum chemistry. The authors freely admit that in molecular resonances which live 10^{-14} sec or less, there is perhaps a quantitative danger in drawing potential curves which depend on strict adherence to the Born-Oppenheimer approximation. For such short lifetimes it is dangerous to talk about potential curves, vibrational levels, etc. On the other hand, as a first approximation in quantitative calculations (as shown by Herzenberg et al.), and in qualitative explanations and predictions of experiment as shown above and in TNG, the usefulness of the quasi-stationary approach and chemical intuitive ideas cannot be denied.

Calculations

Calculations were done on CE1, CE2, and SP resonances. For CE1, the quasivariation method of TW is adequate, as evidenced by the results published in TW. However, to calculate the CE2 and SP resonances, the stabilization method must be used. Hence a basis set for use in the stabilization method must be constructed which is physically reasonable and insures convergence (stabilization) with as few functions as possible.

The calculations were done with the diatomic molecule program of Harris (1960) and Taylor and Harris (1963, series), modified to include the quasivariation and stabilization methods. In this program, trial functions are composed of linear combinations of products of one electron orbitals, so the one electron orbital basis is what is sought for the stabilization method, as used here.

For a homonuclear diatomic molecule, suitable molecular orbitals are defined as

$$\begin{aligned} \phi_r(\delta, \alpha; nmvp) = \exp[-\delta\xi + iv\varphi] \xi^n [(\xi^2 - 1)(1 - \eta^2)]^{|v|/2} \cdot \eta^m \left\{ \exp[-\alpha\eta] \right. \\ \left. + (-1)^k \exp[\alpha\eta] \right\} \end{aligned} \quad (1)$$

where ξ , η , φ are the prolate spheroidal coordinates; δ , α are non-linear variable parameters; n , m are integer exponents; v is the

azimuthal quantum number; p defines gerade or ungerade symmetry of the orbital; r indexes the root of the chosen symmetry which most corresponds to the particular orbital ϕ_r . The exponent k is used to produce the g or u symmetry defined by p through the relation $k = m + p + |v|$ where p is even for g and odd for u. A complete discussion may be found in the theses of either of the authors.

A more compact notation

$$r\lambda_p = \phi_r(\delta, \alpha; nmvp) \quad (2)$$

is now possible, and will be used in the following discussion. As example,

$$1\sigma_g = \phi_1(\delta, \alpha; 0000), \quad 1\sigma_u = \phi_1(\delta, \alpha; 0001), \quad \text{and} \quad 1\pi_u = \phi_1(\delta, \alpha; 00\pm 11).$$

Note that (1) is a highly flexible function with two variable non-linear parameters.

One possible choice of basis would be a set of orbitals as near H_2^+ orbitals as possible, and the functions (1) can be selected to give an excellent representation of these orbitals. For example, at $R = 2.0$ au ($1 \text{ au} = .52917 \text{ \AA}$), the equilibrium separation for the ground state of H_2^+ , a $1\sigma_g$ orbital of the type (1) gives an energy only 0.00002 Hartree above the exact energy as determined by Bates, Ledsham, and Stewart (1953). A basis of this type would be ideal for electron- H_2^+ scattering calculations, but for the target H_2 and calculations on CE resonances a slight modification causes faster stabilization. The basis was actually chosen by the following steps:

1. For a particular internuclear separation R , the best

$1\sigma_g H_2^+$ orbital is found. As is known, this gives an

excellent representation of the innermost orbital of the excited H_2 states which is desirable since core-excited resonances in the field of the excited H_2 states are to be studied.

2. A $1\sigma_g'$ orbital is then added and holding $1\sigma_g$ fixed, is minimized to make the best one term ground state of H_2 . Due to the fixed H_2^+ orbital, this one configuration H_2 result is not the best that could be achieved with the diatomic program.
3. $1\sigma_u$ and $1\pi_u$ orbitals are found by minimization in the field of the $1\sigma_g H_2^+$ orbital to make the best one term $3,1\Sigma_u^+$ and $3,1\pi_u$ states of H_2 .
4. Higher orbitals $2\sigma_g, 3\sigma_g \dots$; $2\sigma_u, 3\sigma_u \dots$; and $2\pi_u, 3\pi_u \dots$ are constructed by minimization of higher roots of the secular equation with the trial function

$$C_1 1\sigma_g 1\lambda_p + \sum_{n=2}^r C_n 1\sigma_g n\lambda_p$$

holding the $1, 2, \dots, r-1$ orbitals fixed.

The sets of orbitals of $\sigma_g, \sigma_u, \pi_u$ symmetry for various values of R which were used in the CE calculations are listed in Tables 4-6.

Products of three of these orbitals are used as a basis for the H_2^- calculations, and in the major configurations representing the CEI resonances the parameters of the outermost orbital were also varied to minimize the energies of the roots which were being stabilized. As all resonance energies (even those obtained by the quasivariation method) were checked for stabilization, this introduced no difficulties.

TABLE 4

 σ_g BASIS ORBITALS

R	No. - nmv													
	$1\sigma_g$ -000		$1\sigma'_g$ -000		$2\sigma_g$ -100		$3\sigma_g$ -300		$4\sigma_g$ -220		$5\sigma_g$ -120		$6\sigma_g$ -400	
	δ	α	δ	α	δ	α	δ	α	δ	α	δ	α	δ	α
1.05	.828891,	.524856	.526042,	.58879	.26193,	.36369	.2112,	0	.19393,	0	.28326,	0	.34924,	0
1.1	.8593,	.5465	.538,	.611	.270,	.379	.21884,	0	.201,	0	.29385,	0	.36273,	0
1.2	.920154,	.589154	.581989,	.655448	.29077,	.408248	.23444,	0	.21529,	0	.31445,	0	.38769,	0
1.3	.978761,	.632081	.616848,	.698727	.30929,	.37115	.24937,	0	.22900,	0	.33448,	0	.41238,	0
1.4	1.035916,	.673943	.651460,	.738934	.327351,	.39282	.26393,	0	.24237,	0	.35401,	0	.43646,	0
1.5	1.091746,	.715231	.686123,	.781250	.34499,	.41399	.27816,	0	.25544,	0	.37309,	0	.45999,	0
1.65	1.173099,	.776848	.738635,	.834097	.37070,	.44480	.29888,	0	.27447,	0	.40090,	0	.49426,	0
1.8	1.252035,	.837942	.783891,	.900291	.39564,	.47477	.31899,	0	.29294,	0	.42787,	0	.52752,	0
1.95	1.328873,	.898702	.870353,	1.067471	.41995,	.52275	.33857,	0	.31092,	0	.95413,	0	.55990,	0
2.1	1.403905,	.959319	.881643,	1.00884	.44363,	.53236	.35769,	0	.32847,	0	.47977,	0	.59151,	0
2.25	1.477368,	1.019904	.924581,	1.058824	.46685,	.56022	.37640,	0	.34566,	0	.50488,	0	.62246,	0
2.4	1.549471,	1.080594	.969630,	1.113074	.48964,	.58757	.39477,	0	.36253,	0	.54498,	0	.65284,	0
2.7	1.690336,	1.202832	1.063269,	1.21261	.53413,	.64096	.43066,	0	.39549,	0	.57766,	0	.71219,	0
3.0	1.82778,	1.326833	1.152866,	1.307184	.57758,	.69310	.46568,	0	.42765,	0	.62463,	0	.77010,	0

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TABLE 5

 σ_u BASIS ORBITALS

R	$1\sigma_u - 000$		$2\sigma_u - 010$		No. - nmv		$3\sigma_u - 210$	$4\sigma_u - 310$	$5\sigma_u - 330$	$6\sigma_u - 430$
	δ	α	δ	α			$\delta(\alpha=0)$	$\delta(\alpha=0)$	$\delta(\alpha=0)$	$\delta(\alpha=0)^*$
1.05	.21729,	.58879	.25995,	.32588			.180	.129	.110	.06042
1.1	.23619,	.62400	.27103,	.35050			.189	.139	.111	.06092
1.2	.27958,	.41937	.29978,	.24054			.205	.153	.111	.06241
1.3	.33152,	.58000	.29499,	.34278			.222	.166	.112	.06389
1.4	.38369,	.57554	.32389,	.34177			.238	.185	.114	.06537
1.5	.42942,	.64413	.34634,	.38552			.258	.196	.116	.06320
1.65	.51134,	.76701	.37185,	.46725			.283	.214	.117	.06320
1.8	.60518,	.87655	.39148,	.54299			.313	.236	.118	.060014
1.95	.68580,	.94750	.40800,	.59700			.337	.258	.119	.060022
2.1	.79160,	1.02830	.43431,	.64647			.365	.277	.120	.063204
2.25	.88569,	1.10406	.45595,	.68393			.390	.300	.121	.063200
2.4	.97944,	1.17610	.47770,	.71655			.414	.327	.122	.063198
2.7	1.16486,	1.33033	.52035,	.78053			.462	.366	.123	.063167
3.0	1.34665,	1.47984	.58694,	.85341			.507	.404	.126	.062900
	*as minimized in quasivariation method.									

No parameters were varied in CE2 or SP calculations once the basis was obtained, as this could lead to disastrous results.

The spin eigenfunctions used were the two three-electron doublets

$$\frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

and

(2)

$$\frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)$$

which can be seen to be $C_1 \alpha\alpha \cdot \beta + C_2 (\alpha\beta + \beta\alpha) \cdot \alpha$ and $C_1 (\alpha\beta - \beta\alpha) \cdot \alpha$ respectively, or therefore one doublet composed of the two electron triplet plus an electron, and one composed of the singlet plus an electron. In the complete open shell treatment (different orbitals for different electrons), both spin doublets are used, and the coefficients corresponding to a particular combination of a spatial configuration (product of three one-electron molecular orbitals) and spin doublet gives an indication of the two electron target state to which the third electron became attached.

The first problem considered was the attempt to improve the results of TW, and to see if two CE1 resonances could be found, rather than the one reported in TW.

Hence the first calculational step was to do a calculation in which $3,1\Pi_u \cdot n\pi_u$ and $3,1\Sigma_g \cdot n\sigma_g$ were mixed and the ground state of H_2 projected out in accordance with the quasivariation method as discussed in TW. The singlet and triplet were automatically mixed by the use of both doublets, so that only two spatial configurations were necessary.

The result was that even though the two electron spatial configurations of the two triplet states were quite close in energy, the three electron states did not mix to six orders of magnitude, and the singlet and triplet parent spin doublets also did not mix. The two-electron Π states have considerably more electron affinity than the Σ states, and both CE1 resonances can thus be formed from $3,1\pi_u$ plus an electron, with the $3,1\Sigma_g$ plus an electron yielding CE2 resonances.

The results presented are actually two-configuration results, because the parent target states $3\pi_u$ and $1\pi_u$ were determined with two configurations, $(C_1 1\sigma_g 1\pi_u + C_2 1\sigma_u 1\pi_g)$. In the singlet Π state, the orbitals $1\pi_u'$, $1\pi_g'$ of Table 6 were used instead of $1\pi_u, 1\pi_g$. C_1 was $\sim .99$ and $C_2 \sim .02$ at all internuclear distances. For the three electron calculation, the $3\pi_u$ orbital was added, and its non-linear parameters varied to minimize the energy. The linear coefficients were unchanged.¹¹

The agreement with experiment demonstrates the efficacy of the one-electron model (product of one-electron functions with small number of configurations). At several R values, additional configurations were added, including higher π_u orbitals, but no additional

¹¹Actually, in a two spatial configuration three electron doublet calculation there are four roots, and four linear coefficients. Since the roots corresponding to the triplet and singlet spin parents do not mix, equivalent results are obtained by using only the doublet $1/\sqrt{6} (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$ with the lower CE1 resonance, and the doublet $1/\sqrt{2} (\alpha\beta\alpha - \beta\alpha\alpha)$ with the upper. Then the linear coefficients are unchanged from the two electron calculations. This provides a useful simplification if the wave functions are to be used for further calculations, such as widths, etc.

binding to the $3,1\Pi_u$ states was obtained. The energy did improve, but only to the extent that the energy of the two-electron states themselves improved. In the interest of computer time, and since the necessary quantitative information for comparison to experiment has been obtained, the two configuration results are considered adequate.

Stabilization was checked by adding configurations of the type $e\cdot H_2(X^1\Sigma_g^+) ^2\Sigma_g^+$, i.e. $\{C_1\sigma_g\sigma_g' + C_2\sigma_u\sigma_u' + C_2\pi_u\pi_u'\} \cdot n\sigma_g$, $n = 2, 3$, etc. The roots corresponding to the CE1 resonances were immediately stable to six figures, the matrix elements between the CE1 resonances and the stabilizing configurations were completely negligible (10^{-8} or less) and the corresponding coefficients in the eigenvector matrix therefore were also negligible. Addition of more $n\sigma_g$ orbitals only served to slightly lower the lowest root to an energy nearer the correct energy of the ground state of H_2 , and inserted unstable roots between the lowest root and the root corresponding to the CE1 resonance (plus meaningless roots above the expected range of the CE2 resonances).

The next step was a quasivariation calculation of the resonance corresponding to $e\cdot ^3\Sigma_u^+$ for comparison to the dissociative attachment experiment.

At large R values, no difficulties were observed, but as R was decreased into the Franck-Condon region, the amount of binding for the third electron also decreased. Somewhere between 1.4 and 1.3 au (R) the binding for the third electron became negligible (0.07 eV or less), and as R was decreased further, the potential curves for the CE1 $^2\Sigma_g^+$ resonances and the $^3\Sigma_u^+$ repulsive state of H_2 were coincident for all

practical purposes. This result is consistent with the model of crossing to form a CE2 resonance in the Franck-Condon region. The stabilization method was applied next. When the roots for R greater than or equal 1.5 au were checked, no change was observed, and the mixing of the stable resonance configurations and the stabilizing configurations was negligible.

However, for smaller R values, the mixing is not negligible, and the roots corresponding mainly to the resonance configurations began to move to higher energy values. Stabilizing configurations of the type $1\Sigma_g^+ \cdot n\sigma_g$ were used, for n from two to seven. The roots corresponding to the resonance usually stabilized once the three stabilizing configurations $1\Sigma_g^+ \cdot \{C_1 2\sigma_g + C_2 3\sigma_g + C_3 4\sigma_g\}$ had been added, however three additional configurations were added at each R as a precautionary check.

The final result obtained was that for the smallest R considered, 1.05 au, the $2\Sigma_g^+$ resonances was 0.2 eV above the $3\Sigma_u^+$ state of H_2 , and that the resonance changed from CE1 to CE2 between 1.4 and 1.5 au.

In these calculations, simple products of one-electron orbitals were again used, with the $3\Sigma_u^+$ of $1\sigma_g 1\sigma_u$ and $2\Sigma_g^+$ of $1\sigma_g 1\sigma_u 6\sigma_u$ from Tables 4-6. For $R \geq 1.5$ au only the one-configuration result and considerably easier to apply for any further calculations. For $R < 1.5$ the CE2 resonance mixes with the stabilizing configurations, so the entire eigenvector is presented for the stable CE2 root at each R in Table 7. The numbers to the left of the table indicate the space-spin configuration, with eleven spatial configurations and the two spin

TABLE 7

EIGENVECTORS FOR STABILIZATION OF ${}^2\Sigma_g$ CE2 ROOTS

Basis Orbitals for Configurations

<u>Configuration</u>	<u>Orbitals</u>
1	$1\sigma_g 1\sigma_u 6\sigma_u$
2	$1\sigma_g 1\sigma_u 5\sigma_u$
3	$1\sigma_g 1\sigma_u 4\sigma_u$
4	$1\sigma_g 1\sigma_u 3\sigma_u$
5	$1\sigma_g 2\sigma_u 6\sigma_u$
6	$1\sigma_g 2\sigma_u 5\sigma_u$
7	$1\sigma_g '1\sigma_u 6\sigma_u$
8	$1\sigma_g '1\sigma_u 5\sigma_u$
9	$1\sigma_g 1\sigma_g '2\sigma_g$
10	$1\sigma_g 1\sigma_g '3\sigma_g$
11	$1\sigma_g 1\sigma_g '6\sigma_g$

TABLE 7

EIGENVECTORS FOR STABILIZATION OF ${}^2\Sigma_g^-$ CE2 ROOTS

NO.	R = 1.05	R = 1.1	R = 1.2	R = 1.3	R = 1.4
1	-0.6333982E 00	-0.6623221E 00	-0.7024906E 00	-0.7379915E 00	-0.7721574E 00
2	0.1626913E-01	-0.1799859E-01	0.8579724E-01	0.1817709E-01	-0.5638126E-02
3	-0.2056712E-02	-0.3541176E-04	-0.3222728E-03	0.2535066E-03	0.9700729E-04
4	0.1891520E 00	0.1512853E 01	0.3306830E 00	0.2490221E 00	0.8967400E 00
5	-0.9952046E-01	0.1312127E-01	-0.1268227E-01	-0.5480240E-02	-0.1467705E-02
6	0.8521528E 00	-0.9879741E 00	0.7026666E 00	0.7172456E 00	-0.1789682E 00
7	0.1507833E-01	-0.1350495E-01	0.1179436E-01	0.1107371E-01	0.1113198E-02
8	-0.8875945E-01	0.1191307E 00	-0.9267284E-01	-0.9645079E-01	0.7124905E-01
9	-0.1821999E-01	0.4141217E-02	-0.1494963E-01	-0.1321234E-01	-0.1930247E-02
10	-0.8573794E-03	0.1171185E-01	0.3093459E-02	-0.5640836E-03	0.8456775E-02
11	-0.109910E-02	0.5381343E-04	-0.3068288E-03	0.2253430E-04	0.4016789E-04
12	0.6099185E-01	-0.4095204E-01	0.7695860E-01	-0.6434724E-02	-0.4359872E-01
13	-0.7874269E-01	0.1958734E-02	-0.8367922E-02	-0.1632179E-02	-0.1277026E-02
14	-0.4382460E-02	0.2753270E-01	-0.1431650E-01	-0.2129001E-01	0.7134695E-02
15	-0.9068978E-03	-0.3336346E-03	-0.1253954E-03	-0.5909892E-04	-0.5025168E-04
16	0.9478928E-01	0.3696452E-01	0.1297499E 00	0.1563071E 00	0.1714288E 00
17	0.2301585E-02	0.7572825E-03	0.4641221E-03	0.1575546E-03	0.1048079E-03
18	0.8518396E-03	0.4349481E-02	0.6908290E-03	0.5431062E-03	0.4017436E-02
19	0.2244960E-02	0.5479784E-02	0.2209623E-02	0.2193951E-02	0.6280439E-02
20	0.1301200E-01	0.6138788E-02	0.1277370E-01	0.1262201E-01	0.7162635E-02
21	0.4948678E-03	0.1796536E-02	0.4397392E-03	0.4378694E-03	0.2232344E-02
22	-0.2010764E-02	-0.3648769E-02	-0.1733061E-02	-0.1460910E-02	-0.3894991E-02
	-0.1559114E-02	-0.5276457E-02	-0.1566271E-02	-0.1584944E-02	-0.6304872E-02

doublets. The odd indices correspond to the combination of a particular spatial configuration and the triplet spin parent $1/\sqrt{6}$ ($2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$), while the even indices correspond to the combinations with the singlet spin parent $1/\sqrt{2}$ ($\alpha\beta\alpha - \beta\alpha\alpha$). The orbitals from Tables 4-6 which make up the eleven configurations are denoted in Table 7. The eigenvectors for the largest, eleven configuration, stabilizing calculation are given rather than a smaller calculation with the same stable root in order to show the relative mixing of the different stabilizing configurations.

These results, and the results of the upper CE1 calculations are presented graphically in Fig. 1. The solid lines correspond to resonances of H_2^- , and the dashed lines to one-electron model calculations of the parent H_2 states. Note that as a result of using a $1\sigma_g H_2^+$ orbital as one of the major elements of the basis set in order to get rapid stabilization of the core-excited resonances, the single configuration calculations for the excited H_2 states are quite good. The CE1 to CE2 crossing point is determined relative to the $^3\Sigma_u^+ H_2$ curve calculated with the same basis.

It is also to be noted that the $^2\Sigma_g^+$ repulsive curve and the $^2\Sigma_g^+$ curve of $e \cdot ^3\Pi_u$ do become nearly tangent at small R values. In fact, from the slopes in Fig. 2, it is possible that they may intersect. Therefore, at two small R values, 1.05 and 1.2 au, the $\sigma_g \sigma_u \sigma_u'$ and $\sigma_g \pi_u \pi_u'$ configurations were mixed again as a check. The off-diagonal elements were $\sim 10^{-8}$ smaller than the diagonal elements in both cases, indicating that whether the non-crossing rule holds or not, the mixing of the two states is so small that if the nuclei possess any kinetic

energy at all, they will follow the diabatic curve rather than the adiabatic, as discussed in the preceding section.

For the stabilization of the two SP resonances of symmetry $^2\Sigma_u^+$ an entirely different procedure was used. Since the SP resonances are physically considered to be a σ_u electron in the field of the slightly polarized ground state, the first step was a full three-configuration variation treatment of the ground state of H_2 . The σ_g^{ls} and $\sigma_g^{ls'}$ are thus not the same as those listed in Table 4, but those which make the best ground state H_2 one term calculation. $\sigma_u^c^{ls}$ and $\sigma_u^c^{ls'}$ were chosen as were π_u^c and π_u^c' as correlating orbitals which minimized the ground state energy. This had to be done at each R point. In general, the orbitals with superscripts c are much more concentrated about the nuclei than the orbitals of Tables 4-6.

The first three-electron wave function was $\left\{ C_1 \sigma_g^{ls} \sigma_g^{ls'} + C_2 \sigma_u^c^{ls} \sigma_u^c^{ls'} + C_3 \pi_u^c 2p_{+1} \pi_u^c 2p'_{-1} \right\} \times \left\{ \sigma_u^c^{ls} + \sigma_u^c^{ls'} \right\}$ and the roots obtained with this calculation were checked for stabilization by adding the σ_u orbitals from Table 5 one at a time to the H_2 ground state function in the first bracket. The trial function above mixed strongly with the first three of these stabilizing configurations, and the roots only began to settle down after the fourth excited σ_u orbital had been added.

This was a very extensive calculation involving a maximum of twelve one-electron orbitals and as many as twenty-one spatial configurations, which with the two spin doublets made a 42×42 secular equation. For this reason, only the energies and qualitative features of the wave functions have been presented. The parameters of all the

orbitals, the eigenvectors, etc. will be furnished upon request.

As in the CE2 cases, addition of stabilizing configurations tended to drive the root corresponding to the SP resonance configuration up, inserting spurious and unstable roots between it and the ground state and improving the ground state root. In contrast, CE1 resonances calculated by the quasivariation method, when stabilizing configurations were added, tended to have their energies slightly lowered, if any energy change occurred at all.

It is interesting to note that another root in the ${}^2\Sigma_u^+$ sequence became approximately stable, at energies about 1.5 - 2.0 eV above the region of the four states ${}^3,1\Pi_u$ and ${}^3,1\Sigma_g^+$ discussed previously. This probably corresponds to a poor calculation of the ${}^2\Sigma_u^+ (\sigma_u \cdot E^1\Sigma_g^+)$ mentioned above as a possible core-excited resonance. The singlet spin parent was definitely more important in the configuration, so it is also possible that the root could correspond to $e \cdot B^1\Sigma_u^+$, however this is felt to be less likely, since the stabilizing configurations tend to push the root up, not down. Further study is necessary to resolve this point, since no configurations other than ${}^2\Sigma_u^+ (X^1\Sigma_g^+) \cdot n\sigma_u$ were included in the trial function, and these cannot be expected to give a good calculation for a CE state, even if a stable root should occur. At present, there is no way of knowing whether the upper root would even remain stabilized upon addition of core-excited configurations, as it did not seem to stabilize as rapidly as the SP root. The semi-stable roots are given in column (f) of Table 3, and the parentheses are used to indicate that they are not considered final or completely

stabilized, but do indicate the possible presence of a CE type resonance near that energy region.

Finally, it should be mentioned that calculations of resonance energies, particularly by the quasivariation method, are fraught with unforeseen and hidden difficulties not encountered in stationary state calculations. First, in every resonance calculated, if the energy was plotted as a function of the "screening parameter" δ of the outermost added orbital, pseudo-minima were encountered, a situation which had not occurred in the case of stationary state calculations with the diatomic molecule program used here. This is probably because variation of δ shifts the maximum electron density of the orbital so that it coincides with the maximum density of higher orbitals, even though the orbital exponents n and m are fixed and do not represent the nodal properties of the higher orbital properly. Each coincidence of electron density maxima would then produce a pseudo-minimum. An example of this is the quasivariation calculation of the $e \cdot {}^3\Pi_u$ resonance. At $R = 3.0$ au, essentially the same energy can be obtained with $\phi_3(.03056, .0; 12-11)$ or $\phi_3(.0632, 0; 42-11)$ and fixed $\phi_1 = 1\sigma_g$ and $\phi_2 = 1\pi_u$. Both ϕ_3 orbitals exhibit false minima for larger δ values.

The second difficulty is with convergence of the two-electron integrals $(ij|1/r|kl)$ when very small δ values are used, particularly in the higher orbitals. Within the limitations set by the program, this problem is purely numerical, caused by the loss of significant figures upon subtraction of large numbers and exponent overflow, underflow and wraparound, and can be surmounted by the use of scaling and/or double precision arithmetic.

Third, there is the amount of physical and chemical intuition required to obtain good results. A poor guess of the major resonance configurations, or a poor trial function for them, may either greatly increase the amount of work necessary to get agreement with experiment, or yield completely meaningless results. The ability to calculate widths and energy shifts would greatly aid in the problem. .

The consequence of these difficulties is that each resonance calculation must be approached as a completely separate problem requiring special, individual handling. There can be no doubt of the fact that the quasivariation and stabilization methods work, as the agreement with experiment reported here shows, but for these and any other calculations of resonant states, extreme caution is necessary. With a well determined basis set, and based on our experience with both methods the stabilization method appears to be preferable for reasons of both flexibility and safety.

The calculations were performed on the Honeywell 800 computer of the University of Southern California Computer Science Laboratory, and the LBM 7094/7044 DCOS equipment of the Jet Propulsion Laboratory. The authors would like to express their appreciation to both institutions for making available the large amounts of computer time which were necessary for these calculations.

CHAPTER IV

SUMMARY

Quasi-stationary methods of calculating the energy of core-excited and single particle resonances and autoionizing states of atoms and molecules are presented both from an intuitive, physical approach and from a formal, rigorous standpoint.

The methods are applied to resonant states of H_2^- , and in the process, a general computer program for calculating the energies and wave functions of diatomic molecules which incorporates both the normal variation method of quantum chemistry for bound states and quasi-stationary methods for resonances has been developed.

The results of the H_2^- calculations are compared to electron scattering experiments.

The diatomic molecule program developed is a modernization of previous methods including several new options, and extended so that calculations can be done for up to twenty electrons. It is fully discussed in a set of Appendices, and a sample calculation on NO^+ is presented as an illustration of the applicability of the program to calculations on large diatomic systems.

APPENDIX I. MATHEMATICAL DETAILS

Wave Function and Coordinate System

The diatomic molecule program discussed in these appendices is a generalized program for calculating the energy of a diatomic molecule within the Born-Oppenheimer approximation, using the variation method with optimization of both linear and non-linear parameters to improve the energy. The mathematical procedures used are an extension and generalization of the programs of Harris (1960), and Taylor and Harris (1963, etc.), and extensive use will be made of these references. The inclusion of the full mathematical treatment, rather than only the outline of its departures from the above methods, is for the purpose of completeness, so that these appendices will contain all the information necessary to understand and to use the diatomic program.

The total wave function is composed of linear combinations of products of one-electron molecular orbitals. These orbitals, ϕ_i , are expressed in prolate spheroidal coordinates, therefore the discussion will begin with the coordinate system and definition of the ϕ_i , and proceed stepwise to the definition of the total wave function.

The prolate spheroidal coordinate system is based on two foci, A and B, where the two nuclei are located. The foci are separated by the internuclear distance R. The coordinates of a point P_i are

(Fig. 8)

$$\begin{aligned}\xi_i &= \left(r_{a_i} + r_{b_i} \right) / R \\ \eta_i &= \left(r_{a_i} - r_{b_i} \right) / R\end{aligned}\quad (1)$$

φ_i = azimuthal angle about the internuclear axis.

The quantity ρ_i , the distance of P_i from the internuclear axis, is also useful, and is expressed as

$$\rho_i = \frac{1}{2} R \left[(\xi^2 - 1)(1 - \eta^2) \right]^{\frac{1}{2}}. \quad (2)$$

The volume element and some differential forms in this system are

$$d\vec{r} = \frac{1}{8} R^3 (\xi^2 - \eta^2) d\xi d\eta d\varphi \quad (3)$$

$$\begin{aligned}\nabla^2 f &= \frac{4}{R^2(\xi^2 - \eta^2)} \left[\frac{\partial}{\partial \xi} \left\{ (\xi^2 - 1) \frac{\partial f}{\partial \xi} \right\} + \frac{\partial}{\partial \eta} \left\{ (1 - \eta^2) \frac{\partial f}{\partial \eta} \right\} \right. \\ &\quad \left. + \frac{(\xi^2 - \eta^2)}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2 f}{\partial \varphi^2} \right] \quad (4)\end{aligned}$$

$$\begin{aligned}\nabla f \cdot \nabla g &= \frac{4}{R^2(\xi^2 - \eta^2)} \left[(\xi^2 - 1) \frac{\partial f \partial g}{\partial \xi \partial \xi} + (1 - \eta^2) \frac{\partial f \partial g}{\partial \eta \partial \eta} \right. \\ &\quad \left. + \frac{(\xi^2 - \eta^2)}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial f}{\partial \varphi} \frac{\partial g}{\partial \varphi} \right] \quad (5)\end{aligned}$$

with the limits $1 \leq \xi \leq \infty$, $-1 \leq \eta \leq 1$, $0 \leq \varphi \leq 2\pi$.

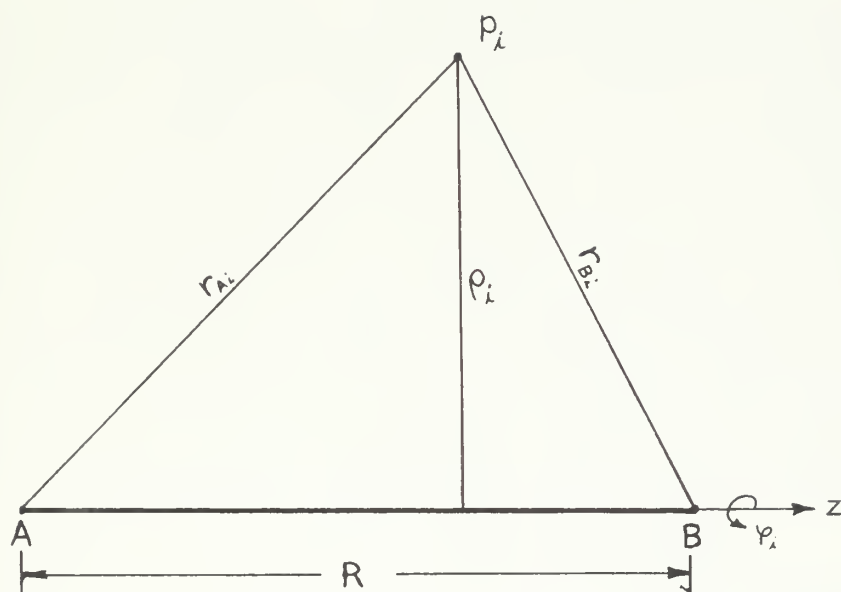


FIGURE 8

PROLATE SPHEROIDAL COORDINATE SYSTEM

The one electron spatial function $\varnothing_i$ is chosen in terms of these coordinates as

$$\begin{aligned}\varnothing_i(\vec{r}_j) &= \exp\left[-\delta_i \xi_j - \alpha_i \eta_j + i v_i \varphi_j\right] \cdot \xi_j^{n_i} \eta_j^{m_i} \cdot (2\rho_i/R)^{|v_i|} \quad (6) \\ &= \varnothing_i(\delta_i, \alpha_i; n_i, m_i, v_i)\end{aligned}$$

where δ_i, α_i are adjustable non-linear parameters which will be determined by the variation method. The δ parameter is a measure of the extent of an ellipse of electron charge density about the two nuclei, and must be positive to assure that the function goes to zero as ξ goes to infinity. The ratio α/δ gives a measure of polarization along the internuclear axis since $\alpha = \delta$ centers the electronic charge on the nucleus at A and $\alpha = -\delta$ centers the charge on the nucleus at B. Intermediate α values allow improvement of the molecular orbital by allowing unsymmetrical, polarized charge distributions.

The exponents n_i, m_i , are restricted to positive integers or zero, and are used to form higher orbitals. Non-zero m_i introduce a node in the perpendicular bisector plane of the internuclear axis. v_i is the azimuthal quantum number, and can assume any integer value, including zero. The $(2\rho_i/R)^{|v_i|}$ factor has been included to provide regularity on the internuclear axis, and because it provides simplifying cancellations in some of the integral expressions to be introduced later.

Atomic orbitals, in particular Slater type orbitals, can be expressed as linear combinations of the elliptical functions $\varnothing_i$ without considerable difficulty, although the number of terms necessary in

the combination goes up quite rapidly as n increases. For example

$$\begin{aligned} 1s_a &= \varnothing(\delta, \delta; 000) \quad , \quad 1s_b = \varnothing(\delta, -\delta; 000) \\ 2s_a &= \frac{1}{2} R [\varnothing(\delta, \delta; 100) + \varnothing(\delta, \delta; 010)] \\ 2s_b &= \frac{1}{2} R [\varnothing(\delta, -\delta; 100) - \varnothing(\delta, -\delta; 010)] \quad . \end{aligned} \quad (7)$$

The remainder of the series can be generated using the fact that from (1) one can express

$$\begin{aligned} r_a &= \frac{1}{2} R(\xi + \eta) \\ r_b &= \frac{1}{2} R(\xi - \eta) \end{aligned} \quad (1')$$

In the homonuclear case, the problem of obtaining gerade or ungerade symmetry of the electronic wave function also presents itself. There are two methods of accomplishing this. One is the passing of the total molecular wave function through the center of inversion, taking the proper linear combination of the function and its inverted counterpart. This method will be discussed later, after introduction of the total wave function. The other is to symmetrize the individual molecular orbitals $\varnothing_i$, actually defining them as σ_g , σ_u , π_u , etc.

The symmetrization of the molecular orbital $\varnothing_i$ is accomplished by inverting it, and taking $\varnothing \pm \vec{i}\varnothing$ with the plus sign for gerade and the minus sign for the ungerade case. The $\vec{i}$ represents the inversion operation, which is equivalent to a reflection in the perpendicular bisector plane of the internuclear axis (interchange of A and B), followed by a rotation of π radians ($\varphi \rightarrow \varphi + \pi$).

Examination of the function $\varnothing$ (Eq. 6) shows that this inversion is accomplished by replacing $\boldsymbol{\eta}$ by $-\boldsymbol{\eta}$ and φ by $\varphi + \pi$, and therefore

$$\varnothing_{g,u} = \left\{ \varnothing(\delta, \alpha; nm\nu) + (-1)^k \varnothing(\delta, -\alpha; nm\nu) \right\} \frac{\sqrt{2}}{2} \quad (8)$$

where $k = p + m + |\nu|$; p representing the parity $\underline{g}$ or $\underline{u}$ desired, with p even for $\underline{g}$ and odd for $\underline{u}$.

Since only certain portions of the function are affected by this operation, it is convenient to rewrite the symmetrized orbitals as

$$\varnothing_i^{g,u}(\delta, \alpha; nm\nu) = e^{-\delta i \xi} \xi^n (2\rho/R)^{|\nu|} e^{i\nu\varphi} \left\{ e^{-\alpha i \boldsymbol{\eta}} + (-1)^k e^{\alpha i \boldsymbol{\eta}} \right\} \boldsymbol{\eta}^m \quad (6')$$

to eliminate excessive computational labor in the actual calculation of the spatial matrix elements.

Now let us define a primitive function $\Phi_j(\vec{r})$

$$\Phi_j(\vec{r}) = \prod_{i=1}^N \varnothing_i(\vec{r}_i) \quad (9)$$

where N is the number of electrons in the system, $\vec{r}_i$ is the position vector of the i^{th} electron, $\vec{r}$ symbolizes collectively the coordinates of all N electrons. The index j will be used to denote a particular spatial configuration after configuration interaction has been introduced.

A single spatial configuration is the antisymmetrized primitive function. Combining it with a spin function θ , one obtains the expression for a single configuration

$$\psi_{j\mu}(\vec{r}, \vec{\sigma}) = \mathcal{A}_n(\Phi_j \theta_\mu) \quad (10)$$

where θ_{μ} is the μ^{th} eigenfunction of S^2 and $\vec{\sigma}$ represents the spin coordinates. Usually in this program one spatial configuration is combined with several spin eigenfunctions comprising a complete spin basis, but depending on the number of closed shell electrons selected in the problem. A more limited spin basis may be used, or a specific spin eigenfunction may be selected which most corresponds to the physical situation. Once a specific problem has been selected (i.e., lowest lying $^3\Sigma$ state of the molecule AB), the number of spin eigenfunctions will be fixed, so for simplicity the word configuration will be used to refer to a spatial configuration, realizing that this spatial configuration may be combined with one or several spin functions.

Defining d as the number of spin functions chosen for a particular problem and m as the number of configurations, the total trial wave function for the l^{th} state of the system becomes

$$\Psi_l(\vec{r}, \vec{\sigma}) = \sum_{i=1}^m \sum_{\mu=1}^d C_{i\mu}^l \psi_{j\mu}(\vec{r}, \vec{\sigma}) \quad (11)$$

where the $C_{i\mu}^l$ are the components of the l^{th} column of the eigenvector matrix determined by diagonalization of the secular equation.

It is now possible to show the method of producing g or u symmetry by inversion of the entire molecule through the inversion center.

The linear combination

$$c_1 \Psi + c_2 \hat{i} \Psi \quad (12)$$

can be considered as a two configuration problem, and the total secular matrix will be

$$\begin{pmatrix} \langle \Psi^* \mathcal{H} \Psi \rangle & \langle \Psi^* \mathcal{H}_i \Psi \rangle \\ \langle i\Psi^* \mathcal{H} \Psi \rangle & \langle i\Psi^* \mathcal{H}_i \Psi \rangle \end{pmatrix} \quad (13)$$

which is a supermatrix of m dxd blocks, and is of the form

$$\begin{pmatrix} A & B \\ B^+ & A \end{pmatrix} \quad (14)$$

since the matrix is Hermitian and $\langle i\Psi^* \mathcal{H}_i \Psi \rangle = \langle \Psi^+ \mathcal{H} \Psi \rangle$.

If this is diagonalized for the energy, both g and u solutions will be obtained due to the form of (12), but it is well known that a matrix of the structure (14) can be diagonalized by the unitary transformation

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \quad (15)$$

and applying this to the supermatrix (13) we obtain the block diagonal matrix

$$\frac{1}{2} \begin{pmatrix} \langle [\Psi + i\Psi]^* \mathcal{H} [\Psi + i\Psi] \rangle & 0 \\ 0 & \langle [\Psi - i\Psi]^* \mathcal{H} [\Psi - i\Psi] \rangle \end{pmatrix} \quad (13')$$

or, taking advantage of (14) again, its simplified equivalent

$$\langle \Psi^* \mathcal{H} (\Psi \pm i\Psi) \rangle \quad (16)$$

Thus we see that Eq. (16) is equivalent to actually taking $\Psi_{gu} = \sqrt{2}/2(\Psi \pm i\Psi)$, but the amount of labor for calculation of

(16) with the proper sign is only about $3/4$ that of calculating and diagonalizing either the g or u block of (13').

The program itself calculates the blocks A and B and then takes the sum or difference as necessary to select the desired symmetry for the molecule.

In the case of Σ states, if pi orbitals are included, plus-minus symmetry must also be considered. This can be handled by replacing v_i by $-v_i$ in each pi orbital in a second configuration and repeating the calculation, and a procedure completely analogous to the above for selecting g or u symmetry can be used to select only the plus or minus linear combinations. Also, one could define a $\theta_{\pm}$ by replacing the $\exp(iv\phi)$ factor in θ by

$$[\exp(iv\phi) \pm \exp(-iv\phi)] \quad (17)$$

in the pi orbitals of a configuration.

Spin and Antisymmetry

In the original diatomic methods (Harris, 1960; Taylor and Harris, 1963), spin and antisymmetry were handled by the method of representation matrices presented by Kotani, et al. (1963). This is an elegant group-theoretical approach in which a complete set of spin eigenfunctions is used as a basis to construct irreducible representation matrices, suitably antisymmetrized, for the n^{th} order permutation group σ_n . The method is completely general, and is particularly adaptable to the case of non-orthonormal spatial orbitals in the complete open shell (different orbitals for different spins)

treatment of the diatomic program.

Unfortunately, the number of mathematical operations in the complete open-shell treatment increases astronomically for larger systems, due to the $n!$ permutations in the group σ_n , and the dimension of each of the set of $n!$ representation matrices. For modern computers, the practical limit appears to be between six and eight electrons. In order to study larger systems, some sort of approximations must be made just to reduce these numbers to something in the realm of manageability.

One possibility is the closing of some or all of the shells (double occupancy). This has the effect of reducing the dimension of the representation matrices to only the invariant part corresponding to the remaining unpaired electrons as is outlined in Kotani, and of reducing the number of permutations necessary, since double occupancy causes linear dependencies in the group σ_n . If there are r paired orbitals, the number of permutations is reduced to $n!/2^r$. As an interim measure, this is helpful, but as n continues to increase, even closing of all the shells fails to reduce the problem to one of manageable size. For example, $16!/2^8$ is still of the order $14!$, and even though the representation matrices are of dimension 1×1 , it is clear that some other approach is necessary.

Another alternative is to introduce spatial orthogonalities, and by knowledge of where these orthogonalities exist, eliminate those permutations which can make no contribution to the total secular equation. This procedure can be used independently of the shell-closing procedure, or they can be used in conjunction. In the

16 electron case mentioned above, by orthogonalizing ten inner shell orbitals in closed pairs, and leaving six open-shell electrons for bonding, the size of the problem is reduced to somewhere between the seven and eight electron complete open-shell problems. This is still rather large, but well within the capabilities of a modern large scientific computer.

Thus one of the aims of this research has been to revise the spin-antisymmetry routines of the older versions of the diatomic program to include options which allow a range between complete open-shell and complete closed shell spin treatments, using any orthogonalities which are introduced or exist naturally to reduce the problem.

Since the formal treatment is fully presented in Kotani (1963), the remainder of this section will be mainly concerned with the actual mechanics of applying the method with all the options as it is done in the edition of the diatomic program presented here. The notation used is chosen to be as consistent with both Kotani and Taylor-Harris as possible. Unless otherwise noted, arguments of functions have been suppressed, and the coordinate number is indicated by position (i.e., $\phi_3(\vec{r}_1) \phi_1(\vec{r}_2) \phi_2(\vec{r}_3) = \phi_3 \phi_1 \phi_2$).

Let the two eigenfunctions of the one-electron operator $\underline{s}_z$ be denoted as α and β , with eigenvalues $1/2$ and $-1/2$, respectively. Then eigenfunctions of the many-electron operator $\underline{S}_z$ can be represented as simple products of α and β ,

$$\Omega = \alpha\alpha \cdots \beta\alpha\beta \cdots \quad (18)$$

with eigenvalue M . In general, there are

$$n_{\Omega} = \binom{N}{\frac{1}{2}N + M} \quad (19)$$

linearly independent simple product functions Ω for a given M value in an N electron problem; and the desired relation

$$\sum_{M=-N/2}^{N/2} \binom{N}{\frac{1}{2}N + M} = 2^N \text{ holds.}$$

The Ω functions are not generally eigenfunctions of $\underline{S}^2$ which, like $\underline{S}_z$, commutes with the Hamiltonian, but a simultaneous eigenfunction of $\underline{S}^2$ and $\underline{S}_z$ can be expressed as

$$\theta_{S,M}^N = \sum_i c_i \Omega_i \quad (20)$$

There are $f_S^N = (1/2N + S) - (1/2N + S + 1)$ functions $\theta_{S,M,k}^N$ $k = 1, 2, \dots, f_S^N$ for given eigenvalues $S(S+1)$ of $\underline{S}^2$ and M of $\underline{S}_z$. In the diatomic program, the coefficients in the above expansion of $\theta_{S,M,k}^N$ are those generated by the method of genealogical construction (Kotani, 1963) which uses the vector coupling formula and the functions α and β to produce

$$\theta_{S,M,k}^N = -\sqrt{\frac{S-M+1}{2S+2}} \theta_{S+\frac{1}{2}, M-\frac{1}{2}; k}^{N-1} \cdot \alpha \sqrt{\frac{S+M+1}{2S+2}} \theta_{S+\frac{1}{2}, M+\frac{1}{2}; k}^{N-1} \beta$$

$$k = 1, 2, \dots, f_{S+\frac{1}{2}}^{N-1} \quad (21)$$

and

$$\theta_{S,M,k}^N = \sqrt{\frac{S+M}{2S}} \theta_{S-\frac{1}{2}, M-\frac{1}{2}; h}^{N-1} \cdot \alpha \sqrt{\frac{S-M}{2S}} \theta_{S-\frac{1}{2}, M+\frac{1}{2}; h}^{N-1} \cdot \beta \quad k = F_{S+\frac{1}{2}}^{N-1} + h$$

$$h = 1, 2, \dots, F_{S-\frac{1}{2}}^{N-1}$$
(21)

This is not a unique choice of $\theta_{S,M,k}^N$, but any other choice may be expressed as a unitary transformation of this set. Katsura (1963), has published a set of all $\theta_{S,M,k}^N$ up to six electrons, and Weltin (1966) has developed a rapid and efficient scheme for generating all $\theta_{S,M,k}^N$ which is limited only by available storage space in the computer.

For the case of d and m both equal to one (one configuration and one spin function), so that the total wave function is represented by Eq. (10). The matrix element of an operator $\underline{O}$, which acts only on spatial coordinates, is

$$\langle \mathcal{A}_n [\phi_1 \theta_1] | \underline{O} | \mathcal{A}_n [\phi_1 \theta_1] \rangle \quad (22)$$

and using the Hermitian property of the antisymmetrizer plus the relation $\mathcal{A}_n^2 = \sqrt{n!} \mathcal{A}_n = \sum_P (-1)^P P$, (22) becomes

$$\sum_P (-1)^P \langle \phi_1 \theta_1 | \underline{O} | P [\phi_1 \theta_1] \rangle \quad (22')$$

where p is the even or odd parity of the permutation P . Since $P = P_r P_\sigma$, Eq. (22') can be separated to obtain

$$\sum_P \langle \phi(\vec{r}) | \underline{O} | \phi(P_r \vec{r}) \rangle \langle \theta(\vec{\sigma}) | (-1)^P \theta(P_\sigma \vec{\sigma}) \rangle \quad (23)$$

where the $(-1)^P$ has been included in the spin integral for convenience. Calculation of the spin integrals yields a set of coefficients $U_\mu(P)$, so that the matrix element can be expressed as

$$\sum_P U_\mu(P) \langle \Phi | \underline{Q} | P\Phi \rangle = \sum_P U_\mu(P) \underline{Q}(P) \quad (24)$$

with the definitions

$$\begin{aligned} \underline{Q}(P) &= \langle \Phi | \underline{Q} | P\Phi \rangle \\ U_\mu(P) &= (-1)^P \langle \theta_\mu | P\theta \rangle \end{aligned} \quad (25)$$

where the permutation is on either the functions or the coordinates in both integrals.

Additional spin functions may be introduced in which case the set $U_\mu(P)$ becomes a matrix of dimension d , where d is the number of spin eigenfunctions in the basis. Thus for one configuration, the matrix element of the operator $\underline{Q}$ becomes a $d \times d$ matrix of the form

$$\sum_P U(P) \underline{Q}(P) \quad (26)$$

where

$$U(P) = [U_{\mu\nu}(P)] = (-1)^P \langle \theta_\mu | P\theta_\nu \rangle \quad (27)$$

The secular equation for the energy is then

$$\sum_P U(P) [\underline{H}(P) - E \underline{S}(P)] = 0 \quad (29)$$

If the complete set of spin eigenfunctions is included ($d = F_S^N$) the matrices $U(P)$ become unitary, irreducible representations of the permutation group, and are exactly the $U(P)$ defined in Kotani (1963) and the Taylor-Harris papers (1960, 1963, etc.).

When spatial configuration interaction is included, the definition of $\underline{O}(P)$ can be expanded to $\underline{O}_{jk}(P) = \langle \phi_j | O | P\phi_k \rangle$, and the total secular matrix (29) becomes an $m \times d$ matrix, composed of $d \times d$ blocks for each $H_{jk}(P)$, $S_{jk}(P)$; $j, k = 1, 2, \dots, m$.

Given the sets $\theta_{S,M,k}^N$, it is now possible to generate the representation matrices $\underline{U}(P)$ systematically, thus completely separating the spin and space parts of the problem, since once generated, the $\underline{U}(P)$ are general for any problem with the same N, S , and M . From Eq. (27)

$$U_{\mu\nu}(P) = (-1)^P \langle \theta_{S,M,\mu}^N | P \theta_{S,N,\nu}^N \rangle \quad (27')$$

and therefore for an arbitrary permutation P , the associated $\underline{U}(P)$ may be generated from a single rectangular matrix $\underline{C}$, which has n_Ω rows and d columns stemming from the expansion of $\theta_{S,M}^N$ in terms of the Ω_i (Eq. 20).

Thus the μ, ν elements

$$\begin{aligned} U_{\mu\nu}(P) &= (-1)^P \left\langle \sum_{i=1}^d C_{i\mu} \Omega_i \mid P \sum_{j=1}^d C_{\nu j} \Omega_j \right\rangle \\ &= (-1)^P \sum_{i=1}^d \sum_{j=1}^d C_{i\mu} \cdot C_{Pj\nu} \langle \Omega_i | \Omega_{Pj} \rangle \end{aligned}$$

where $P\Omega_j = \Omega_{Pj}$, which is a member of the complete Ω set, and due to the orthogonality of the Ω

$$U_{\mu\nu}(P) = (-1)^P \sum_i \sum_j C_{i\mu} C_{Pj\nu} \delta_{i,Pj}.$$

This is repeated for all μ, ν ; $1 \leq \mu \leq d$, $1 \leq \nu \leq d$ to make the full matrix. The α 's and β 's are easily represented in a digital computer

as 0's and 1's, making the operation $P\Omega_j$ and the checking of $\delta_{i,Pj}$ relatively simple.

For a truncated θ_k basis, depending on the functions which are omitted, certain rows in $\underline{C}$ may have only zero elements ($C_{i\mu} = 0$; $1 \leq \mu \leq d$). If so, those rows are omitted, and the multiplication by zero handled implicitly by the Kronecker δ function for computational convenience.

Since it is now possible to form the matrix $\underline{U}(P)$ for any arbitrary P , the next requirement is a method of generating all the permutations P of the group σ_n . Harris (1960) devised a simple algorithm for systematically generating all $N!$ permutations of the full group, optimizing mathematical operations and scan time.

Consider the arbitrary permutation P . It is desired to generate the succeeding permutation Q in as few operations as possible and such that Q is not a repetition of some permutation generated prior to P .

Read the numbers in P from left to right until the first increase occurs (i.e., first number which is larger than the one to its left). The position of this number is called the pivot position. Interchange the number in the pivot position with the largest number to its left which is less than the number itself. Simply copy (leave unchanged) everything to the right of this position. Then arrange all numbers to the left of the pivot position in ascending order. The result is the permutation Q . If there was no increase, all permutations have been generated.

For example, consider P represented by $\underline{i}/1 \ \underline{j}/2 \ \underline{k}/3 \ \underline{l}/4 \ \dots \ s/n$, with $i > j < k > l$, and $i > k$. The pivot position is 3, occupied by k . By the inequalities, j is the largest number less than k , so j and k are interchanged and $\underline{l} \dots \underline{s}$ are left as they were. Then i is greater than k , so they are rearranged in ascending order, and the resulting Q representation is $\underline{k}/1 \ \underline{i}/2 \ \underline{j}/3 \ \underline{l}/4 \ \dots \ s/n$.

The parity is easily determined by inspection of the canonical number of the position immediately to the left of the pivot position, $c_{\text{piv}-1}$. If $c_{\text{piv}-1} [\text{Mod. } 4]$ is less than two, the parity of Q is opposite to that of P , and if it is ≥ 2 , the parity of Q is the same as that of P . In the example above $c_{P-1} = 2$, and $2[\text{Mod. } 4] = 2$, therefore Q and P have the same parity.

Table 8 gives a full numerical illustration of the results of the above techniques for the case of a complete open-shell three-electron doublet, with two spin functions $\theta_{\frac{1}{2}, \frac{1}{2}, 1}^3$ and $\theta_{\frac{1}{2}, \frac{1}{2}, 2}^3$, and six permutations in the order they are generated.

The above procedure is general for any number of θ functions, but if closed shells are introduced and the dimension of the θ set reduced concomitantly, the $U(P)$ become linearly dependent. (The expression "closed shells" is to be interpreted as strict double occupancy.) It is still possible to generate all the $N!$ permutations and $U(P)$, but a much more favorable computational situation would occur if a way of generating only the linearly independent subset of P and $U(P)$ could be determined.

TABLE 8

SPIN-PERMUTATION MATRICES FOR THE
OPEN-SHELL THREE ELECTRON DOUBLET

$\theta_{\frac{1}{2}\frac{1}{2}1}^3 = \frac{1}{\sqrt{6}} \quad (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$ $\theta_{\frac{1}{2}\frac{1}{2}2}^3 = \frac{1}{\sqrt{2}} \quad (\alpha\beta\alpha - \beta\alpha\alpha)$														
Eigenvector matrix $\underline{C}$ <table> <tr> <th>$\Omega \backslash \theta$</th><th>1</th><th>2</th></tr> <tr> <td>$\alpha\alpha\beta$</td><td>$2/\sqrt{6}$</td><td>0</td></tr> <tr> <td>$\alpha\beta\alpha$</td><td>$-1/\sqrt{6}$</td><td>$-1/\sqrt{2}$</td></tr> <tr> <td>$\beta\alpha\alpha$</td><td>$-1/\sqrt{6}$</td><td>$-1/\sqrt{2}$</td></tr> </table>			$\Omega \backslash \theta$	1	2	$\alpha\alpha\beta$	$2/\sqrt{6}$	0	$\alpha\beta\alpha$	$-1/\sqrt{6}$	$-1/\sqrt{2}$	$\beta\alpha\alpha$	$-1/\sqrt{6}$	$-1/\sqrt{2}$
$\Omega \backslash \theta$	1	2												
$\alpha\alpha\beta$	$2/\sqrt{6}$	0												
$\alpha\beta\alpha$	$-1/\sqrt{6}$	$-1/\sqrt{2}$												
$\beta\alpha\alpha$	$-1/\sqrt{6}$	$-1/\sqrt{2}$												
P	p	U(P)												
1 2 3	(+)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$												
2 1 3	(-)	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$												
1 3 2	(-)	$\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$												
3 1 2	(+)	$\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$												
2 3 1	(+)	$\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}$												
3 2 1	(-)	$\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$												

For r closed shell pairs of electrons, the θ basis becomes

$$\theta_{S,M,k}^N = \theta_{S,M,k}^{N-2r} (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \cdots (\alpha\beta - \beta\alpha) \left(\frac{\sqrt{2}}{2} \right)^r$$

$$k = 1, 2, \dots, f_S^{N-2r} \quad (30)$$

and there are $N!/2^r$ linearly independent matrices and permutations in the subgroup of σ_N . The generation of the $U(P)$ is the same as before, except using the reduced θ basis so the problem becomes one of generation of only the linearly independent subset of permutations.

The Harris algorithm can easily be adapted to this problem. If an auxiliary permutation vector R is introduced, such that the vector P contains the actual function (coordinate) numbers, and R contains a set of dummy indices in which the closed shells are represented by duplicated numbers, a linearly independent subset can be generated by doing the permutation-generating scan over R , performing the same operations on P , and using P to generate $U(P)$ and $\underline{O}(P)$.

For example, a six electron triplet might have the form

$$\frac{\sqrt{2}}{4} (\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$$

and the corresponding initial P and R would be

$$P - 1 \ 2 \ 3 \ 4 \ 5 \ 6$$

$$R - 1 \ 2 \ 3 \ 3 \ 5 \ 5 \ .$$

As an even more complete example, consider the three electron doublet with one closed shell pair, whose spin eigenfunction is $\theta_{\frac{1}{2}\frac{1}{2}2}^3$, and whose P and $U(P)$ can be represented by the $U_{2,2}$ elements of the six permutation matrices of Table 8. Here it is seen that of the set of six permutations, if electrons one and two are the same, 123-213, 132-231, and 312-321 are equivalent, and moreover, that the 2,2 elements of their matrices are also identical. Thus selection of three of the non-equivalent permutations with their respective matrices would

only have the effect of multiplying the total secular equation by a constant, in this case $1/2$.

Setting the initial P and R as 123 and 113 respectively, the sequence of permutations becomes

$$\begin{array}{lll} P - 123(+) & 231(+) & 321(-) \\ R - 113(+) & 131(+) & 311(-) \end{array}$$

so we see that the search over R will produce $3!/2 = 3$ non-equivalent permutations and using P to generate $U(P)$ and $\underline{O}(P)$ will produce the desired secular equation.

The preceding techniques can be applied automatically by the present modification of the diatomic program. The case of orthogonal functions is slightly less easy to generalize, and thus requires some planning on the part of the user before proceeding to the computation stage. No modification of the program is necessary, only careful preparation of the input data cards.

A completely orthogonal spatial basis would have non-zero elements only in the case of pairwise interchanges and the identity permutation.

For any other case, one must consider the spatial orthogonalities and the coordinate operators. Clearly, the set of permutations used must include all possibilities of one or two electron operators contributing to the secular equation. Thus, any permutation of a configuration which produces no more than two zero factors in $S(P)$ must be included, and conversely, any permutations which may be seen to include three or more overlap factors which are zero may be excluded.

In a many configuration calculation, the configuration with the minimum number of orthogonalities controls the exclusion of permutations.

This option has been included in the program by allowing the user to generate a set of permutations particular to his problem by hand and instruct the permutation generating routine of the program of the specific limitations placed upon it. The program will generate any additional permutations as required and produce the reduced set of $U(\mathbf{P})$ delineated by the permutations.

As an example, see the NO^+ calculation reported elsewhere in this work (page 140ff.) which was included specifically for the purpose of illustrating the use of this option.

A word of caution is necessary here. When a complete spin basis is used, and the full $N!$ set of matrices $U(\mathbf{P})$ is thus generated, the ordering of the one-electron spatial functions in each configuration is energetically immaterial, since re-ordering is a unitary transformation, and the eigenvalues will not be changed. However, the eigenvectors will reflect the re-ordering transformation, and they will be changed accordingly.

On the other hand, if a truncated spin basis is used, whether all $N!$ $U(\mathbf{P})$ are generated or not, the eigenvalues will be dependent on the order, and for best results, the spatial functions must be ordered to correspond physically to the ordering of the α and β in the spin functions.

If one takes advantage of the orthogonality options, obviously the functions must be ordered to correspond with the set of hand-

generated permutations, and the ordering must be preserved in all configurations of a multi-configuration problem.

Matrix Elements

To produce the secular equation (29), the spatial integrals $H(\mathbf{P})$ and $S(\mathbf{P})$ must be evaluated. From Eq. (25), these are recognized as

$$S_{jK}(\mathbf{P}) = \left(\phi_j | P \phi_K \right) \quad (31)$$

and

$$H_{jK}(\mathbf{P}) = \left(\phi_j | \mathcal{H} | \phi_K \right) \quad (32)$$

where

$$\mathcal{H} = \frac{Z_A Z_B}{R} + \sum_{i=1}^n h_i + \sum_{i \leq j < i}^n \frac{1}{r_{ij}} \quad (33)$$

and

$$h_i = -\frac{1}{2} \nabla_i^2 - \frac{Z_A}{r_{iA}} - \frac{Z_B}{r_{iB}} \quad (33')$$

Z_A and Z_B are the charges of nuclei A and B, separated by the distance R . The distances r_{xy} are the distances between particles x and y . Atomic units are used, with energies in Hartrees (1 au = 27.21 eV), and length in Bohrs (1 au = .52917 Å).

Since no term of $\mathcal{H}$ includes the coordinates of more than two electrons, $H(\mathbf{P})$ is reducible to sums of products of one- and two-electron integrals, and obviously $S(\mathbf{P})$ can be expressed as a simple product of one-electron overlap integrals.

Thus the matrices

$$(i|h|j) = \int \phi_i^*(\vec{r}_1) h_1 \phi_j(\vec{r}_1) d\vec{r}_1 \quad (34)$$

$$(i|j) = \int \phi_i^*(\vec{r}_1) \phi_j(\vec{r}_1) d\vec{r}_1 \quad (35)$$

and

$$(ij|1/r|kl) = \int \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_2) \frac{1}{r_{12}} \phi_k(\vec{r}_1) \phi_l(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (36)$$

can be calculated and stored, and the necessary elements combined to make $H(\mathbf{P})$ and $S(\mathbf{P})$ for a given $\mathbf{P}$.

Expanding in terms of the coordinates (Eq. 1), the one-electron integral $(i|h|j)$ separates into a kinetic energy integral and two nuclear attraction integrals,

$$\begin{aligned} (i|h|j) = & \left(i \left| -\frac{1}{2} \nabla^2 \right| j \right) - \frac{2}{R} (Z_A + Z_B) \left(i \left| \frac{\xi}{(\xi^2 - \eta^2)} \right| j \right) \\ & + \frac{2}{R} (Z_A - Z_B) \left(i \left| \frac{\eta}{(\xi^2 - \eta^2)} \right| j \right) . \end{aligned} \quad (37)$$

With the form of the wave function (6), all the one-electron integrals may be expressed in closed form in terms of the functions (Kotani, 1963)

$$A_n(\delta) = \int_1^\infty t^n \exp[-\delta t] dt \quad (38)$$

$$B_n(\alpha) = \int_{-1}^1 t^n \exp[-\alpha t] dt . \quad (39)$$

The integrals for non-zero v may be compactly handled if the definitions of (38) and (39) are extended to

$$A_n^v(\delta) = \sum_{k=0}^{|v|} \binom{|v|}{k} (-1)^{v-k} A_{n+2k}(\delta) \quad (38')$$

$$B_n^v(\alpha) = \sum_{k=0}^{|v|} \binom{|v|}{k} (-1)^k B_{n+2k}(\alpha) \quad (39')$$

Then, by direct substitution of the function (6), followed by separation of variables and integration over φ , it may be found that

$$(i|j) = \frac{\pi R^3}{4} \delta(v_i, v_j) \left[A_{n+2}^v(\delta) B_m^v(\alpha) - A_n^v(\delta) B_{m+2}^v(\alpha) \right] \quad (40)$$

$$\left(i \left| \frac{\xi}{(\xi^2 - \eta^2)} \right| j \right) = \frac{\pi R^3}{4} \delta(v_i, v_j) A_{n+1}^v(\delta) B_m^v(\alpha) \quad (41)$$

$$\left(i \left| \frac{\eta}{(\xi^2 - \eta^2)} \right| j \right) = \frac{\pi R^3}{4} \delta(v_i, v_j) A_n^v(\delta) B_{m+1}^v(\alpha) \quad (42)$$

where $n = n_i + n_j$, $m = m_i + m_j$, $\delta = \delta_i + \delta_j$, $\alpha = \alpha_i + \alpha_j$ and $v = v_i = v_j$.

The kinetic energy integral is more tedious, but after some manipulation can be converted to the form

$$\begin{aligned} \left(i \left| -\frac{1}{2} \nabla^2 \right| j \right) = & -\frac{1}{8} \delta(v_i, v_j) \int d\vec{r} \left(\frac{2\rho}{R} \right)^{2|v|} \\ & \times \left[\emptyset_i^{\circ} \nabla^2 \emptyset_j^{\circ} + \emptyset_j^{\circ} \nabla^2 \emptyset_i^{\circ} - 2 \nabla \emptyset_i^{\circ} \cdot \nabla \emptyset_j^{\circ} - 4 \left(\frac{v}{\rho} \right)^2 \emptyset_i^{\circ} \emptyset_j^{\circ} \right] \end{aligned}$$

where $\emptyset_i^{\circ} = \zeta^{n_i} \eta^{m_i} \exp[-(\delta_i \zeta + \alpha_i \eta)]$, and after substitution of (6)

becomes

$$\begin{aligned}
 & (i | -\frac{1}{2} \nabla^2 | j) \\
 &= \frac{\pi R^3}{4} \delta(v_i, v_j) \times \left[-\frac{1}{2R^2} \right] \left\{ \left[\delta'^2 A_{n+2}^v(\delta) - 2(\delta' n' + \delta) A_{n+1}^v(\delta) \right. \right. \\
 & \quad \left. \left. + 2\delta' n' A_{n-1}^v(\delta) + (n-n'^2) A_{n-2}^v(\delta) \right] B_m^v(\delta) \right. \\
 & \quad \left. - \left\{ \alpha'^2 B_{m+2}^v(\alpha) - 2(\alpha' m' + \alpha) B_{m+1}^v(\alpha) + 2\alpha' m' B_{m-1}^v(\alpha) + (m-m'^2) B_{m-2}^v(\alpha) \right\} A_n^v(\delta) \right. \\
 & \quad \left. + \left\{ n'^2 + n - \delta'^2 - n'^2 - m + \alpha'^2 \right\} A_n^v(\delta) B_m^v(\alpha) - 4v^2 \left\{ A_{n+2}^{v-1}(\delta) B_m^{v-1}(\alpha) - A_n^{v-1}(\delta) B_{m+2}^v(\alpha) \right\} \right]
 \end{aligned} \tag{43}$$

where $n' = n_i - n_j$, $m' = m_i - m_j$, $\delta' = \delta_i - \delta_j$, and $\alpha' = \alpha_i - \alpha_j$.

The coefficients of $A_n^v(\delta)$ and $B_m^v(\alpha)$ vanish when negative indices would be required, and correct results are obtained when these undefined values of A_n^v and B_m^v are assumed to be zero.

The symmetrized orbitals (6') are easily included by noting that

$$\begin{aligned}
 & (i_{g,u} | \underline{0} | j_{g,u}) \\
 &= (i | \underline{0} | j) + (-1)^{k_i + k_j} (i' | \underline{0} | j') + (-1)^{k_j} (i | \underline{0} | j') + (-1)^{k_i} (i' | \underline{0} | j)
 \end{aligned}$$

where i' is the function $\emptyset(\delta, -\alpha; nmv)$. It is clear that

$$B_m^v(-\alpha) = (-1)^m B_m^v(\alpha)$$

therefore it is possible by collecting terms to define the auxiliary integral

$$B_m^{v'}(\alpha, \alpha') = 2\delta \left[0, m+k_i+k_j \pmod{2} \right] \left\{ B_m^v(\alpha) + (-1)^{k_j} B_m^v(\alpha') \right\}$$

and since in each of the integrals (40-43) all terms involving m are of the same parity, the Kronecker delta function can be factored out, leaving the integrals in exactly the same form, except using

$B_m^{\prime\vee}(\alpha, \alpha')$ rather than $B_m^{\vee}(\alpha)$. This method is not unique, but it has the advantages that it requires less memory storage, and reduces the amount of actual computation by about one-third.

The $A_n(\delta)$ are obtained by the recursion formula

$$A_n(\delta) = A_0(\delta) + \frac{n}{\delta} A_{n-1}(\delta) \quad (44)$$

with $A_0(\delta) = 1/\delta e^{-\delta}$. The $B_m(\alpha)$ could also be generated recursively, using the formula (Kotani, 1963)

$$B_m(\alpha) = \frac{1}{\alpha} \left\{ (-1)^m e^{\alpha} - e^{-\alpha} + n B_{n-1}(\alpha) \right\}$$

but Corbato (1956) has developed a method which does not involve subtraction of terms of similar magnitude and therefore is more accurate. The B_m are calculated in conjunction with related functions used in the two-electron integrals.

Because all the orbitals in this problem are of a single parametric form, there is but one type of 2-electron integral in our work, rather than the usual plethora of hybrid, coulomb, exchange, and one-center integrals. To evaluate the 2-electron integral $(ij|1/r|kl)$, we use Neumann's expansion (1878) of $1/r_{12}$,

$$\begin{aligned} \frac{R}{2r_{12}} = & \sum_{u=0}^{\infty} \sum_{\sigma=-\mu}^{\mu} (-1)^{\sigma} (2\mu + 1) \left[\frac{(\mu - |\sigma|)!}{(\mu + |\sigma|)!} \right]^2 \\ & \times P_{\mu}^{|\sigma|}(\xi_-) Q_{\mu}^{|\sigma|}(\xi_+) P_{\mu}^{|\sigma|}(\eta_1) P_{\mu}^{|\sigma|}(\eta_2) \exp[i\sigma(\phi_1 - \phi_2)], \end{aligned} \quad (45)$$

where ξ_+ and ξ_- mean the larger, and smaller, respectively, of

ξ_1 and ξ_2 . $P_\mu^{|\sigma|}$ and $Q_\mu^{|\sigma|}$ are associated Legendre functions.

On substituting Eq. (45), and introducing the wave functions, Eq. (6), we perform first the integrations over φ_1 and φ_2 . If we let

$$\begin{aligned} v_K - v_i &= \sigma_1, \\ v_l &= v_j = \sigma_2 \end{aligned} \quad (46)$$

the φ dependence of the integral is $\exp i(\sigma_1 + \sigma)\varphi_1 + i(\sigma_2 - \sigma)\varphi_2$, so the integral vanishes unless

$$\sigma_1 + \sigma_2 = 0, \quad (47a)$$

in that case the sum over σ collapses to the single value (or its negative)

$$\sigma = |\sigma_1| = |\sigma_2|. \quad (47b)$$

Henceforth we shall use σ to mean the value given by Eqs. (47a)-(47b). The φ integrations then cause the removal of the σ summation, and the change of the lower limit of the μ summation to σ , while contributing to $(ij|1r|kl)$ a factor $4\pi^2 \delta(\sigma_1, -\sigma_2)$.

We next consider the factors involving $(\xi^2 - 1)$ and $(1 - \eta^2)$. When the contributions from all four wave functions are collected, we have

$$\left[(\xi_1^2 - 1)(1 - \eta_1^2) \right]^{\frac{1}{2}|v_i| + \frac{1}{2}|v_K|} \left[(\xi_2^2 - 1)(1 - \eta_2^2) \right]^{\frac{1}{2}|v_j| + \frac{1}{2}|v_l|}.$$

When we do the ξ and η integrations, we will find it convenient to write this as

$$\left[(\xi_1^2 - 1)(1 - \eta_1^2) \right]^{\frac{1}{2}\sigma + \tau_1} \left[(\xi_2^2 - 1)(1 - \eta_2^2) \right]^{\frac{1}{2}\sigma + \tau_2},$$

since the $1/2\sigma$ power can be naturally associated with the Legendre functions. In general, the τ value to be associated with any two orbitals, say ϕ_u and ϕ_v , will be $\tau = 1/2(|v_u| + |v_v| - |v_u - v_v|)$, and in particular

$$\begin{aligned}\tau_1 &= \frac{1}{2} \left(|v_i| + |v_k| - \sigma \right) \\ \tau_2 &= \frac{1}{2} \left(|v_j| + |v_l| - \sigma \right) .\end{aligned}\quad (48)$$

Note that these definitions imply that τ is a positive integer or zero.

We are now prepared to consider the integrations over ξ_1 and ξ_2 . It is evident that the integrand cannot be factored to separate the coordinates (ξ_1, η_1) from (ξ_2, η_2) because of the presence of the Legendre functions involving ξ_+ and ξ_- . This situation can be alleviated somewhat by using a slight generalization of a formula published by Ruedenberg (1951). The formula we need can be expressed as

$$\begin{aligned}(-1)^\sigma (2\mu + 1) \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 P_\mu^\sigma(\xi_-) Q_\mu^\sigma(\xi_+) g_\mu^1(\xi_1) g_\mu^2(\xi_2) \\ = \int_1^\infty d\chi G_\mu^1(\chi) G_\mu^2(\chi)\end{aligned}\quad (49)$$

where $g_\mu^\gamma(\xi)$ and $G_\mu^\gamma(\chi)$, $\gamma = 1$ and 2 , are related by

$$\begin{aligned}G_\mu^\gamma(\chi) &= \left\{ (2\mu + 1) [(\mu + \sigma)! / (\mu - \sigma)!] \right\}^{\frac{1}{2}} \\ &\times \left[P_\mu^\sigma(\chi) (\chi^2 - 1)^{\frac{1}{2}} \right]^{-1} \int_1^\chi d\xi P_\mu^\sigma(\xi) g_\mu^\gamma(\xi).\end{aligned}\quad (50)$$

This transformation may be applied whenever all the operations indicated are meaningful. The exponential dependence of the wave functions is sufficient to guarantee the utility of Eqs. (49) and (50).

Summing both sides of Eq. (49) from $\mu = \sigma$ to ∞ , we have, with suitable definition of $g_\mu^\gamma(\xi)$, an expression for $(ij|1/r|kl)$. Examining the result of the substitution of Eqs. (45) and (6) into $(ij|1/r|kl)$, it may be seen that

$$g_\mu^\gamma(\xi) = [(\mu-\sigma)!/(\mu+\sigma)!] \int_{-1}^1 d\eta (\xi^2 - \eta^2) \exp(-\delta_\gamma \xi - \alpha_\gamma \eta) \\ \times P_\mu^\sigma(\eta) (\xi^2 - 1)^{(\sigma/2)+\tau_\gamma} (1 - \eta^2)^{(\sigma/2)+\tau_\gamma} \xi^{n_\gamma} \eta^{m_\gamma} \quad (51)$$

Here, $\delta_1 = \delta_i + \delta_k$, $\delta_2 = \delta_j + \delta_l$, with corresponding definitions for α_γ , n_γ , and m_γ . The η integrations appearing in Eq. (51) are all of the same general form. Define

$$i_\mu^\sigma(m, \alpha, \tau) = \left\{ (2\mu + 1) [(\mu - \sigma)!/(\mu + \sigma)!] \right\}^{\frac{1}{2}} \\ \times \int_{-1}^1 d\eta P_\mu^\sigma(\eta) \exp(-\alpha\eta) \eta^m (1 - \eta^2)^{(\sigma/2)+\tau} \quad (52)$$

and Eq. (51) may be rewritten

$$\left\{ (2\mu+1) [(\mu+\sigma)!/(\mu+\sigma)!] \right\}^{\frac{1}{2}} g_\mu^\gamma(\xi) \\ = \exp(-\delta_\gamma \xi) \xi^{n_\gamma} (\xi^2 - 1)^{(\sigma/2)+\tau_\gamma} \left[\xi^2 i_\mu^\sigma(m_\gamma, \alpha_\gamma, \tau_\gamma) - i_\mu^\sigma(m_\gamma+2, \alpha_\gamma, \tau_\gamma) \right] \quad (53)$$

The integrals defined in Eq. (52) are related to spherical Bessel functions, and also to the $B_n(\alpha)$. The B_n can be expressed (Corbato, 1956) in terms of the i_μ^σ as

$$B_n = \sum_{\mu=0,1}^n{}' \frac{n! (2_{\mu+1})^{\frac{1}{2}}}{(n-\mu)!!(n+\mu+1)!!} i_{\mu}(0, \alpha, 0) \quad (54)$$

where $\sigma = 0$, or if $v \neq 0$, since σ is necessarily zero for non-zero one-electron integrals, $v_i = v_j = \tau$, so the binomial summation of (39') can be avoided by using the relation

$$B_n^v(\alpha) = \sum_{\mu=0,1}^n{}' \frac{n! (2_{\mu+1})^{\frac{1}{2}}}{(n-\mu)!!(n+\mu+1)!!} i_{\mu}(0, \alpha, \tau) . \quad (54')$$

In both expressions the prime on the summation sign indicates taking only every other term such that the highest μ value = n , and the double factorial is $n!! = n(n-2)(n-4)\dots(2 \text{ or } 1)$.

For the symmetrized one electron orbitals, the $i_{\mu}^{\sigma}(m, \alpha, \alpha', \tau)$ become

$$i_{\mu}^{\sigma}(m, \alpha, \alpha', \tau) = 2\delta_{[0, \text{mod}_2(m+\kappa_1+\kappa_j+\mu-\sigma)]} \left\{ i_{\mu}^{\sigma}(m, \alpha, \tau) + (-1)^{\kappa_j} i_{\mu}^{\sigma}(m, \alpha', \tau) \right\} \quad (55)$$

since

$$P_{\mu}^{\sigma}(-\eta) = (-)^{\mu-\sigma} P_{\mu}^{\sigma}(\eta) .$$

The next step is to substitute Eq. (53) into Eq. (50), and perform the ξ integration. When doing so, it is convenient to define another set of integrals

$$K_{\mu}^{\sigma}(n, \delta, \tau, x) = \left[P_{\mu}^{\sigma}(x) (x^2 - 1)^{\frac{1}{2}} \right]^{-1} \times \int_1^x d\xi P_{\mu}^{\sigma}(\xi) \exp(-\delta\xi) \xi^n (\xi^2 - 1)^{(\sigma/2)+\tau} \quad (56)$$

in terms of which Eqs. (53) and (50) yield

$$G_{\mu}^{\gamma}(\mathbf{x}) = K_{\mu}^{\sigma}(n_{\gamma} + 2, \delta_{\gamma}, \tau_{\gamma}, \mathbf{x}) i_{\mu}^{\sigma}(m_{\gamma}, \alpha_{\gamma}, \tau_{\gamma}) - K_{\mu}^{\sigma}(n_{\gamma}, \delta_{\gamma}, \tau_{\gamma}, \mathbf{x}) i_{\mu}^{\sigma}(m_{\gamma} + 2, \alpha_{\gamma}, \tau_{\gamma}). \quad (57)$$

To show more clearly the role of the wave functions in $G_{\mu}^{\gamma}(\mathbf{x})$, we shall from now on use the notation $(u|G_{\mu}(\mathbf{x})|v)$ to mean a form like $G_{\mu}^{\gamma}(\mathbf{x})$, but with n_{γ} replaced by $n_u + n_v$, etc.

Recapitulating the earlier discussion in more explicit form, we obtain the result that the two-electron integral has been reduced to the form

$$(ij|1/r|kl) = \left(\frac{\pi R^3}{4}\right)^2 \left(\frac{2}{R}\right)^{\delta(\sigma_1, -\sigma_2)} \int_1^{\infty} d\mathbf{x} \sum_{\mu=\sigma}^{\infty} (i|G_{\mu}(\mathbf{x})|k)(j|G_{\mu}(\mathbf{x})|l). \quad (58)$$

The integral over $\mathbf{x}$ in Eq. (58) is now to be evaluated numerically.

Using values of the integrand at points $\mathbf{x}_K$, the integral can be written

$$(ij|1/r|kl) = \left(\frac{\pi R^3}{4}\right)^2 \left(\frac{2}{R}\right)^{\delta(\sigma_1, -\sigma_2)} \sum_K w_K \sum_{\mu=\sigma}^{\infty} (i|G_{\mu}(\mathbf{x}_K)|k)(j|G_{\mu}(\mathbf{x}_K)|l),$$

where w_K is a weight factor. Defining

$$(w_K)^{\frac{1}{2}} (i|G_{\mu}(\mathbf{x}_K)|j) = (i|G_{\mu K}|j), \quad (59)$$

Eq. (58) becomes

$$(ij|1/r|kl) = \left(\frac{\pi R^3}{4}\right)^2 \left(\frac{2}{R}\right)^{\delta(\sigma_1, -\sigma_2)} \sum_K \sum_{\mu=\sigma}^{\infty} (i|G_{\mu K}|k)(j|G_{\mu K}|l). \quad (60)$$

The number of terms one must keep in the sum over μ may be estimated by studying the behavior of the K and i integrals, Eqs. (52) and (54). By far the most important quantities affecting the convergence of the sum are found to be $|\alpha_1|$ and $|\alpha_2|$, larger values of which correspond to slower convergence. In fact, for $\alpha = 0$ the series reduces to a finite number of terms. Since the speed of computation depends on the number of terms, we actually compute a number chosen for each integral after examining its $|\alpha_1|$ and $|\alpha_2|$. As a rough indication, we use an average of 13 terms for $|\alpha| = 10$, and 19 terms for the maximum value, $|\alpha| = 19.9$.

Details of the calculation of the integrals $i_{\mu}^{\sigma}(m, \alpha, \tau)$ and $K_{\mu}^{\sigma}(n, \delta, \tau, x)$ can be found in Appendices II and III of the Harris work (1960).

Parameter Variation Scheme

The trial wave function can be improved both by selection of the best set of linear coefficients through diagonalization of the secular equation, and by minimization of the energy with respect to the non-linear parameters δ_i and α_i , $i = 1, 2, \dots, N_0$. In this discussion, the word energy signifies the total electronic energy of the desired root of the secular equation.

In the earlier modifications of the diatomic program, a pure network search was used, because there was no way of knowing at that time whether more sophisticated searching routines would get trapped in false minima.

An analysis of the energy dependence on the non-linear parameters has now become possible since large numbers of calculations on many types of systems have been performed using the stepwise search.

Several representative calculations have been analyzed, including ground states, excited states, heteronuclear and homonuclear molecules, atoms, and resonant states. Some definite features were observed, leading to the following conclusions:

1. In true bound states of atoms or molecules, both ground and excited, the dependence of the energy on the non-linear parameters is smooth. No false or pseudo-minima were found in any of the extensive number of calculations checked.
2. The energy is considerably more sensitive to the choice of the δ parameter for a given orbital than the choice of the α of the same orbital.
3. The parameters of the orbitals, if originally chosen in a "reasonable" fashion (not such that the maximum density of a σ_{2s} lies inside the maximum density of a σ_{1s} , for example), are relatively independent of each other.
4. Resonant states exhibited false minima in the δ parameter of the added electron (outermost orbital), and the α dependence was nearly flat. The energy is particularly sensitive to very small variations of δ in the region nearest the minimum.

Thus it is now possible to use a more sophisticated parameter searching routine, as long as some option is retained to avoid the false minima in resonances (or other false minima if they are suspected).

Consider the case of a set of parameters chosen so that the energy is near the minimum value attainable with the trial function being used. Let x_i represent the non-linear parameters, either δ_i or α_i , E_0 = the energy calculated with the set x_i , and y_i the set of increments ($x_i - a_i$). The energy can be expanded as

$$E_x = E_0 + \sum_i \left(\frac{\partial E}{\partial x_i} \right)_0 y_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 E}{\partial x_i \partial x_j} \right)_0 y_i y_j + \dots \quad (61)$$

and the minimum will be attained if

$$\frac{\partial E}{\partial x_i} \equiv 0 \quad (62)$$

Dropping all terms of order greater than two in the expansion and substituting the minimization condition, we obtain the set of equations

$$\left(\frac{\partial E}{\partial x_i} \right)_0 + \sum_j \left(\frac{\partial^2 E}{\partial x_i \partial x_j} \right)_0 y_j = 0 \quad (63)$$

which can be solved for the revised set of parameters if $1/2(n+2)(n+1)$ calculations of the energy are done (n is the number of parameters in the set $\bar{x}_i$). This can be seen to be the equivalent of assuming the energy dependence on each parameter to be a parabola, and finding the minimum of the set of parabolae which are linked by the cross terms

$x_i x_j (i = j)$. Ransil (1960) applied a similar procedure to diatomic molecule calculations and found that if the parameters were nearly independent, this method converged in three to five passes through the set of $1/2(n+2)(n+1)$ energy calculations, using the new $\bar{y}_i$ to determine a revised E_0 .

However, if the parameters are independent, or nearly so, the effect of the cross terms should be negligible, and an equivalent result should be obtained if each of the parameters $\bar{x}_i$ were fitted to a parabola holding the other parameters fixed, and the set $\bar{x}_i$ stepped through one by one. This requires only $3n$ energy calculations per pass through the set $\bar{x}_i$, and as there are two non-linear parameters per orbital, produces a nice reduction in the amount of work necessary to minimize the energy with respect to the non-linear parameters if there are two or more orbitals.

This process, with a slight modification to be described below, is the one used in the present diatomic program. It also converges quite rapidly, with two passes normally minimizing the energy to five or six figures.

The actual scheme works slightly differently for variation of $\bar{\delta}_i$ and of $\bar{\alpha}_i$. Since the initial set of δ parameters may be quite far from the optimum set, each parameter is stepped with a large step size in the forward or backward direction until there exists an $E_i(\delta_i)$ which is less than both $E_{i-1}(\delta_{i-1})$ and $E_{i+1}(\delta_{i+1})$, where i indexes the number of the calculation. If the energy continues to improve in a certain direction, the step size is increased to hasten finding

the δ_{i+1} which causes the energy to turn back upwards. The optimum parameter δ is then determined by fitting to the parabola passing through the lowest three points E_i , E_{i+1} , and E_{i-1} . In this process, more than three energy calculations may be required before fitting, but it has the advantage that the first pass through the δ set always produces a revised E_0 which is quite close to the true minimum of the functional.

Since the α dependence is more flat, the search procedure for the first pass through the α parameters only makes three calculations per α , at the values α_0 , $1/2 \alpha_0$, and $3/2 \alpha_0$. On subsequent passes through the α set, the method is the same as for δ .

After one complete pass through all the δ and α which are to be optimized, the step size is reduced to one-third the starting value and the process is repeated.

In the case of resonances, a stepwise search over the parameters of the outermost electron is still necessary in order to avoid becoming trapped in a pseudo-minimum. This option is included in the program by setting a tag which both demands a stepwise search in the forward direction, and determines the number of steps to be taken. As in the previous modifications of the program, the programmer-user must apply his experience and physical intuition to determine the magnitude of the step size and the number of steps which will locate the parameter near the true minimum without becoming trapped. After each of the designated outer orbital parameters has been linearly searched by this method, the optimum set of stepwise parameters is

re-minimized by the parabola search method.

In all of the above procedures, the search may be terminated externally by setting of a sense switch. In the parabolic search, variation of a particular parameter is eliminated in subsequent passes if the program determines that the energy is relatively independent of it. This can also be done externally by proper preparation of the input cards.

If the program is not terminated externally, it proceeds automatically through the list of parameters to be varied, reducing the step size after each pass until it is lower than a preset threshold step size. At this time, a final calculation is made with the optimum set of parameters and the search for the problem is terminated.

In this modification of the program, it is also possible to treat the internuclear distance R as a parameter, in that after completion of a parameter search at one R value, R can be incremented or decremented and the problem restarted. In this case, the non-linear parameters are scaled by $R_{\text{new}}/R_{\text{old}}$, and the $\bar{\alpha}$ search assumes that it has already made one pass.

Thus, if computer time is available, it is possible to calculate the entire potential curve for a particular molecule in one run, stepping through R and minimizing the energy in terms of the non-linear parameters at each desired R value.

APPENDIX II. DETAILS OF THE DIATOMIC MOLECULE PROGRAM
AND INSTRUCTIONS FOR ITS USE

Overall Logic

General Comments

The diatomic molecule program as written is designed for a 32,768 word high-speed computer with at least four peripheral storage units (tape or disc). It is in the FORTRAN IV language, with no machine language programs, in order that maximum machine-to-machine compatibility be achieved. To the same end, no advantage has been taken of special features of some machines, such as reading tapes backward, multiple entries to subroutines, availability of additional peripheral equipment, etc. Variable dimension statements and logical IF statements have been used.

A rather extensive list of options has been included, in order to do the most general diatomic molecule problem without changing the program internally, and still allow some special treatment of specific problems.

The program is designed to calculate the energy and electronic wavefunction of heteronuclear or homonuclear diatomics. In the homonuclear case, gerade or ungerade symmetry can be achieved either through the use of symmetry adapted one-electron orbitals, or by an

option of reflecting the entire molecular function through the inversion center and taking the proper linear combination of the original and inverted functions.

The spin portions are set to handle the complete open-shell (different orbitals for different spins) problem automatically for up to a 28×28 set of representation matrices, which includes the full, eight electron case. By a change in the input deck, up to twenty electrons may be handled with partially or completely closed shells. The spin routines are also arranged so that advantage can be taken of the reduction in numbers of permutations which can be introduced through spatial orthogonalities, by never generating those permutations which would make no contribution to the secular equation.

The one-electron spatial functions are two-centered elliptical orbitals. A transformation routine is included which allows linear combinations of these functions prior to diagonalization, so that both fixed and variable linear coefficients are possible. Space is available for up to sixteen functions and a 16×16 transformation matrix.

Non-linear parameter search options include a combination network-gradient search and a pure stepwise network search, with the ability to vary one function independently, or two functions simultaneously. Through appropriate tagging, one, both, or neither of the two non-linear parameters of a particular function may be varied, and the search routine has the ability to set these tags internally if the energy is found to be relatively independent of the parameter being varied.

Through the use of sense switches, the programmer may also externally terminate the search, skipping immediately to the final output routine with the best set of parameters achieved up to that time.

The internuclear distance may also be varied, with a new calculation of the electronic wave function, including non-linear parameter variation at each R value.

Thus the program presented here is a compromise among generality, speed, efficiency, and size. For selected specific types of problem, some of the options may be removed if desired for further optimization of these factors.

Block Structure

The logic flow of the program is divided into five main branches, which are handled by an input and controlling main program. The function of each of these branches is as follows:

Branch 1 - SETUP Branch

Reads auxilliary tape identifiers, loads permanent data tables for integral calculations, makes spin-permutation tape. Re-entered only if spin problem is changed. All output from this branch is labeled COMMON blocks or on tape (disc).

Branch 2 - INTEGRAL Branch

Controls calculation of all one- and two-electron spatial integrals. Makes integral table tape of indices, parameters, one-electron integrals, and $G_{i,k}(x,\mu)$. Combines all $G_{i,k}$

with $G_{j,l}$ to make tape of all two-electron integrals. Upon exit, all one- and two-electron integrals are on tape for subsequent iterations, and in fast memory for combining with spin.

Branch 3 - MATRIX Branch

Applies transformation to spatial integrals if required.

Combines spatial integrals with spin matrices from tape to make total secular equation. In homonuclear case with total molecular inversion option, secular equation is block diagonalized in this branch.

Branch 4 - SEARCH Branch

Solves secular equation. Varies non-linear parameters as desired, prints intermediate output. If parameter search not completed, return to INTEGRAL branch, otherwise proceed to OUTPUT branch.

Branch 5 - OUTPUT Branch

Prints final output, including total secular equation, eigenvalues, eigenvectors, converted energies and spatial configurations. If program was cut externally by sense switch, punches new input deck for convenient restart.

Control of Storage and Internal Overlays

Of prime importance is the control of the working space inside fast memory. In the various branches, and inside the branches, data is overlaid when it is no longer needed. In order to prevent destroying information which will be required later in the calculation,

an understanding of the places and times that these overlays occur is mandatory if modifications are to be introduced, if it is desired to use certain routines as "black boxes" for entirely different calculations, or if the program is to be updated.

To facilitate bookkeeping, all fast storage is in four labeled COMMON blocks. A description of the contents of these blocks and the overlays which occur in them follows.

/SPACE/ - 309 words. Contains most problem definition data as described in input deck summary below, plus

ITX - iteration counter. 1-first pass; 2-intermediate passes;
3-final pass

FPAR $\emptyset$ - best set of non-linear parameters, stored from FPAR
as determined

E $\emptyset$ - best energy, corresponding to calculation with FPAR $\emptyset$

NO - tag for parameter being searched. 1-delta; 2-alpha

MO - function number of parameter being searched, i.e.,
search over FPAR(NO,MO)

ICTAG - 64 locations available for additional tags as desired.

Data in this block is generally permanent, with the only overlays being resetting of tags, changing parameters, etc.

/DATBLS/ - 759 words. Permanent information. Not changed during run. See below for details.

/CIJ/ - 268 words. Transformation matrix and tags. Matrix is recalculated if NOTRF > $\emptyset$, but not overlaid by other data.

/WORK/ - 12,518 words. Main working area. Overlaid by all branches as follows:

1. SETUP - overlays controlled by subroutine SPIN. Used to contain all information for generation of spin tape. Completely destroyed upon exit from spin routine.
2. INTEGRAL - during making of one-electron tapes and combination to make two-electron tape, /WORK/ is composed of two arrays JTA and JTB, dimensioned $146\cancel{0}\times 4$, and the one-electron integrals S1 and H1, singly dimensioned at 136 words each. S1 and H1 are stored as calculated. The two-electron tape is read upon completion, storing the H2 integrals over JTA and JTB. Array JTB is used as temporary storage by the integral routines ONEL, BANDI, and GLIST. 289 locations available in array named DUMBO.
3. MATRIX - at entry, contains H2 (9317), SPRI, HPRI (S1, H1 of INTEGRAL branch), transformed one-electron sets renamed S1, H1, one 28×28 spin matrix, one permutation, and room for the total S, H stored triangularly ($18\cancel{0}6$ words). At exit, H2 is overlaid by the total secular equation OVP, HAM which is S, H unpacked and stored as full two dimensioned arrays. Array named DOM has 19 locations available.
4. SEARCH - six 42×42 matrices for secular equation and eigenvectors, including two copies of secular equation, one for printing if desired, and one which is destroyed during diagonalization. Several vectors dimensioned 42 for

eigenvalues, etc. Array named FINK has 1760 locations available.

5. OUTPUT - essentially same as SEARCH, except FINK contains only 1672 locations.

Limitations

The following limitations must be observed to prevent premature termination of the calculation by built-in error checks:

Maximum number of one-electron functions	16
Maximum number of electrons in IPER	20
Maximum number of spin eigenfunctions θ	28
Maximum number of spin functions Ω	--
Maximum dimension of secular equation	42
Largest n_i, m_i	4
Largest α_i	19.9
Smallest δ_i	.01

Error Messages

Error messages may occur during calculation if the internal checks are positive. Some of these errors will not cause premature termination of the program, and others will. The following is a summary of these error messages, their causes, and the action taken by the program:

1. WRONG PERM TAPE xxxxxx xxxxxx

The identification tag on the spin-permutation tape does not agree with the tag required by the formula

$$JCODE = 1000*N + 10*LOSH + MULT$$

calculated when the problem is defined. This can be due to a mis-positioned tape or to having mounted the wrong tape. The program repositions the tape and either continues or exits, depending on the condition of a recheck. The first number in the message is the desired number, and the second is the number read from the tape.

2. SEC EQN TOO BIG xxxx

The dimension of the secular equation requested by the input parameters (NCONXND) is larger than 42.

3. INDICES DONT CHECK xx xx xx xx xx xx

Subroutine INTEG has detected that the indices on tape KR and the indices in the integral calculation loop do not correspond. The indices L1, I and J are printed in pairs with the supposed L1, I, and J read from tape KR.

4. BANDI - NO CONVERGE

The μ summation of Eq. (60) did not converge in 36 terms or less.

5. BANDI - PARAMS OUT xx xx xx xx

One or more parameters are out of range. The four numbers printed are τ , m , $|\sigma|$, and M , where τ , m , and $|\sigma|$ are defined in Appendix I and $M = 28 + |\alpha|/1.95$, which defines a dimension and cannot exceed 60.

6. GLIST - GENERAL ERR

Self-explanatory

7. GLIST - PARAMS OUT xxxxxx xx xx

Parameters out of range in subroutine GLIST. The three numbers are δ , n , and $LM = L4 + n + 2\tau + 2$, where δ and n are explained in Appendix I, and LM is a calculated dimension which cannot exceed 45.

8. ENERGY.LT.MIN

The calculated energy is lower than the experimental or test energy punched on the title card. An exit is made to the OUTPUT branch, after which a new calculation may be started if more input cards are present.

9. GR.SRCH SEEKS MAX

The gradient or parabola search is seeking a maximum rather than a minimum. This is an information message only.

10. END SRCH OF FCN xx xx

The energy has been found to be independent of a particular parameter, and the tag has been set to discontinue the search of this parameter. Its indices are printed for information.

11. OVRIAP NOT POS DEF xxxxxxx xx xx

The overlap matrix is not positive definite. If it is positive semi-definite, this is an information message only. If the magnitude of the negative diagonal element is less than 10^{-7} , the program assumes that the matrix is numerically positive semi-definite, deletes the row and column corresponding to this element in both the S and H matrices, and

continues. This results in an eigenvalue of 10^{26} which can easily be seen. If the negative diagonal element is greater than 10^{-7} in magnitude, the program makes an error exit.

Specific Programs and Subroutines

A short summary of the programs follows. Those routines which are marked by asterisks are discussed in detail below the summary. The logic of the unmarked routines can be followed without difficulty in the program listings themselves.

<u>TITLE</u>	<u>TYPE</u>	<u>BRANCH</u>	<u>PURPOSE</u>
DIAT	M	MAIN	DATA INPUT & MAIN CONTROLLING PROGRAM
SETUP	S	SETUP	INITIALIZATION OF TABLES, ETC.
TABLE*	S	SETUP	FIXES PERMANENT DATA BLOCK, POINTS, WEIGHTS, ETC.
SPIN*	S	SETUP	PREPARES TAPE OF SPIN-PERMUTATION MATRICES
CONFIG*	S	SETUP	READS CONFIGURATION TABLES INTO LCON (config. array)
HDG	S	MAIN/ OUTPUT	PRINTS TITLE PAGES IN OUTPUT
INTEG*	S	INTEGRAL	CONTROLS PRODUCTION OF ALL SPATIAL INTEGRALS
ONEL*	S	INTEGRAL	MAKES ONE-ELECTRON INTEGRALS FROM BANDI OUTPUT
BANDI	S	INTEGRAL	MAKES B,A,AND I INTEGRALS
GLIST	S	INTEGRAL	MAKES $G_{ik}(x)$ FROM ξ INTEGRATION AND I INTEGRALS
TWOEL	F	INTEGRAL	COMBINES G_{ik} WITH G_{jl} TO MAKE $(ij 1/r_{12} kl)$
COMBIN	S	INTEGRAL	CONTROLS CALLING OF TWOEL FUNCTION

<u>TITLE</u>	<u>TYPE</u>	<u>BRANCH</u>	<u>PURPOSE</u>
TAPE	S	INTEGRAL	READS AND WRITES INTEGRAL TAPE
MATRIX*	S	MATRIX	COMBINES SPACE AND SPIN PARTS TO MAKE TOTAL SECULAR EQUATION
TXFORM	S	MATRIX	PREPARES TRANSFORMATION MATRIX FOR SPATIAL FUNCTIONS
TRANS	S	MATRIX	APPLIES TRANSFORMATION TO ONE-ELECTRON INTEGRALS
TRX	F	MATRIX	APPLIES TRANSFORMATION TO TWO-ELECTRON INTEGRALS
SEARCH	S	SEARCH	ENERGY CALCULATION AND PARAMETER SEARCH LINK
D23CHO	S	SEARCH	SOLVES GENERAL EIGENVALUE PROBLEM AND ORDERS ROOTS, VECTORS
EIG	S	SEARCH	JACOBI MATRIX DIAGONALIZATION
OUTPUT	S	OUTPUT	PRINTS FINAL OUTPUT
PMA	S	OUTPUT	PRINTS MATRICES AS SQUARE OR TRIANGULAR ARRAYS

*TABLE - FIXES PERMANENT DATA BLOCK, POINTS, WEIGHTS, ETC. Sub-routine TABLE generates D1, DD1, and DD2 for BANDI and GLIST. Their definitions are:

$$D1_{i,j} = (i-1)!(2j-1)/[(i-j)!!(i+j-1)!!] \quad (64)$$

$$DD1_{i,j} = [(i+j-2)!(2i-1)/(i-j)!]^{\frac{1}{2}} \quad (65)$$

and

$$DD2_{i,j} = [(i+j-1)(i-j+1)/(4i^2-1)] , \quad (66)$$

and they are calculated recursively.

The numerical quadrature points and weights are read in this routine. They are read as data rather than loaded as a permanent

BLOCK DATA Subroutine to allow the use of several different quadrature formulae, with different numbers of points. Space is available for up to a forty point integration rule. The integral limits $(1, \infty)$ are transformed to $(0, 1)$, so the points are in increments of $1/x$ and the weights are

$$w_k = x_i w_i^{\frac{1}{2}} / (x_i^2 - 1)^{\frac{1}{2}} \quad (67)$$

where

w_k is the value punched on the input cards, $WT(K)$

x_i is the i^{th} point in POINT

w_i is the tabulated weight from the numerical quadrature rule.

Card decks have been prepared and are available for the original 34-point Newton-Cotes formula used by Harris and Taylor (1963, etc.), and for 16, 20, 24, and 32 point Gaussian formulae. Table 9 gives a comparison of two-electron integrals for various δ values using these formulae. The 34-point formula should be used in any check calculations which attempt to duplicate the results of the old Taylor-Harris or Taylor calculations.

*SPIN - PREPARES TAPE OF SPIN-PERMUTATION MATRICES. Subroutine SPIN applies the methods described in Appendix I, (84 ff.) to generate the permutations IPER, and their $ND \times ND$ representation matrices $UMAT(I, J)$. A given permutation (read or calculated) is applied to the spin product functions ISP, and an ordering vector ISSPM is created such that if the permutation is denoted by P, and P on $ISP(I)$ yields $ISP(K)$, then $ISSPM(K) = I$. Using this ordering vector,

TABLE 9

COMPARISON OF ANALYTIC AND NUMERICAL
TWO-ELECTRON INTEGRALS

δ	Analytic	32 Pt Gaussian	24 Pt Gaussian	20 Pt G	16 Pt G	³⁴ Pt Newton-Cotes
.005	$.312496 \times 10^{-2}$	$.357119 \times 10^{-2}$	$.382192 \times 10^{-2}$	$.273463 \times 10^{-2}$	$.116467 \times 10^{-2}$	$.1114793 \times 10^{-1}$
.010	$.624967 \times 10^{-2}$	$.591432 \times 10^{-2}$	$.669905 \times 10^{-2}$	$.782367 \times 10^{-2}$	$.721512 \times 10^{-2}$	$.1114921 \times 10^{-1}$
.02	$.124973 \times 10^{-1}$	$.126405 \times 10^{-1}$	$.120132 \times 10^{-1}$	$.119074 \times 10^{-1}$	$.140510 \times 10^{-1}$	$.118887 \times 10^{-1}$
.04	$.249787 \times 10^{-1}$	$.249477 \times 10^{-1}$	$.251654 \times 10^{-1}$	$.251091 \times 10^{-1}$	$.237301 \times 10^{-1}$	$.181768 \times 10^{-1}$
.08	$.498302 \times 10^{-1}$	$.498276 \times 10^{-1}$	$.498209 \times 10^{-1}$	$.497302 \times 10^{-1}$	$.503481 \times 10^{-1}$	$.505149 \times 10^{-1}$
.16	$.986616 \times 10^{-1}$	$.986615 \times 10^{-1}$	$.986571 \times 10^{-1}$	$.986810 \times 10^{-1}$	$.985717 \times 10^{-1}$	$.996227 \times 10^{-1}$
.25	.151281	.151281	.151282	.151278	.151306	$.150251 \times 10^{-1}$
.32	.189865	.189865	.189864	.189866	.189852	.189674
.5	.277261	.277261	.277261	.277260	.277254	.277393
.75	.367753	.367753	.367753	.367753	.367738	.367721
1.0	.425974	.425974	.425974	.425974	.425957	---
1.5	.479705	.479705	.479705	.479705	.479686	---

$$\text{UMAT}(I, L) = \left[\sum_{J=1}^{\text{NISP}} \text{USET}(I, J) \cdot \text{USET}(L, K) \right] \cdot \text{SIG}$$

where USET is the spin eigenvector matrix, $K = \text{ISSPM}(J)$, and $\text{SIG} = \pm 1$, the parity of the permutation P.

*CONFIG - READS CONFIGURATION TABLES INTO LCON. Subroutine

CONFIG is simply a reading routine using variable dimension statements which allows maximum use of the 150 words allocated for the configuration table LCON. LCON is dimensioned as an $\text{NCON} \times \text{N}$ matrix rather than with fixed dimensions, so that 75 two-electron, 50 three-electron, etc. configurations are possible. CONFIG reads, prints, or punches LCON in this type of storage. Note, however, that the maximum dimension of the total secular equation is 42×42 , and that $\text{NCON} \times \text{ND}$ may not exceed this limit.

*INTEG - CONTROLS PRODUCTION OF ALL SPATIAL INTEGRALS. The

second major branch is controlled by subroutine INTEG, which handles the calculation of all spatial integrals. This is done in two steps, the first being the calculation of the one-electron integrals Sl_{ij} , Hl_{ij} and G_{ij} for all i and J ($i \geq j$), and second, taking all possible combinations of G_{ij} with $\text{G}_{i'j'}$ to make the two-electron integrals.

To save storage space, and due to the symmetry of the spatial one-electron matrix elements, the Sl_{ij} and Hl_{ij} sets are stored as vectors containing only the $1/2 n(n+1)$ elements of the lower triangle. The (i, j) element of the matrix can be looked up by

$$\text{INDX}(I, J) = \text{MIN}(I, J) + [(\text{MAX}(I, J) \cdot (\text{MAX}(I, J) - 1))] / 2$$

where $\text{MIN}(I, J)$ is the lesser of i and j , and $\text{MAX}(I, J)$ the greater.

By the same token, a double application of this method allows storage of the two-electron integrals in a single vector H2, containing $1/2 m (m+1)$ elements where $m=1/2 n (n+1)$. In this case, the φ integrations are done later.

A single (i,j) integral table requires 1460 words — 19 words for indices, parameters, and one-electron integrals, and the (40×36) $G_{ij}(x,\mu)$ matrix (also treated as a one-dimensional vector by INTEG — unpacked only in GLIST and TWOEL).

For optimization of input-output time, since these tables (named JTA, JTB, or ZG1 in the routine) must be stored on tape or disc, they are generated in blocks of four, and written on tape KW each time four sets have been completed. One to three blank tables may be written in the last block of four in order to make the total number of tables a multiple of four. If a previous integral tape KR exists (i.e., second and subsequent passes of parameter variation scheme), the pertinent blocks of tables are read from this tape before actual integral calculation begins.

Subroutine ONEL is called for generation of each table. Upon return, the Sl_{ij} , and Hl_{ij} are extracted, normalized, and stored in fast memory for subsequent branches.

The second, combination, stage of INTEG uses COMBIN and TWOEL. Every block of four tables must be combined with every other block, making ten or sixteen two-electron integrals depending upon whether a block is combined with itself or another block.

To effect this combination of G_{ik} tables from the tape, the following logic is used to minimize tape-handling time, which experience has shown to be the rate-controlling step in the entire energy calculation.

Let there be NTOT blocks of four tables. The last ($NTOT^{th}$) block is still intact in fast memory. This block is combined with itself while the tape is rewound. The tape is then read forward and blocks 1,2,3....., NTOT-1, are combined with NTOT. At this point, the $NTOT^{th}$ block has been completely combined, so NTOT is reduced by one. The tape is now read backwards (actually, two BACKSPACES followed by a read to remain in the FORTRAN IV language), combining the new $NTOT^{th}$ block with all the blocks down to block one. This process is continued back and forth dropping a block each time as it has been fully combined until all the blocks have been eliminated. For example, if there are five blocks of four tables, the logic would produce the following order of block combination:

55,51,52,53,54,44,34,24,14,11,12,13,33,23,22.

Since the single index of each two-electron integral is calculated from the i,j,k,l indices in the tables and written on the two-electron integral tape KINT along with the integral, this peculiar order of calculation has no effect.

Upon completion of the combinations, the two-electron integrals are read into fast memory for the next branch.

*ONEL - MAKES ONE-ELECTRON INTEGRALS FROM BANDI OUTPUT. Sub-routine ONEL is called by INTEG with a particular i and j , and a designated table of 1460 words. ONEL compares the parameters in the

table (if an old table exists) with the current set and either returns if there has been no change, or calculates a new set of one-electron integrals and G vector through calls to BANDI and GLIST.

The layout of each individual table is as follows [Greek symbols as defined in Appendix I (ff.)]:

WORD DEFINITION

- 1 NLP(1) - $v_i - v_j = \sigma$
- 2 NLP(2) - $(|v_i| + |v_j| - |\sigma|)/2 = \tau$
- 3 NLP(3) - $m_i + m_j = m$
- 4 NLP(4) - number of steps necessary for convergence of I integrals
 (i.e., upper limit of μ summation)
- 5 NLP(5) - $n_i + n_j = n$
- 6 NLP(6) - $m_i - m_j = m'$
- 7 NLP(7) - $n_i - n_j = n'$
- 8 NOTA(1) - I
- 9 NOTA(2) - J
- 10 EPOT - potential energy term, independent of R
- 11 INDX - $J + I(I-1)/2$ ($J \leq I$)
- 12 Maximum length of table - $19 + JMAX \cdot (NLP(4))$
- 13 FLP(1) - $\delta_i + \delta_j = \delta$
- 14 FLP(2) - $\delta_i - \delta_j = \delta'$
- 15 FLP(3) - $\alpha_i + \alpha_j = \alpha$
- 16 FLP(4) - $\alpha_i - \alpha_j = \alpha'$
- 17 S1(I,J)
- 18 EKIN - kinetic energy term, independent of R

WORD DEFINITION

19 GINY - point at infinity for G_{ij} , zero except in 34-point Newton-Cotes integration (see Harris, 1960 - Eq. 115)

20 G_{ij} - integral table, of length $JMAX \cdot (NLP(4) - |\sigma|)$

*MATRIX - COMBINES SPACE AND SPIN PARTS TO MAKE TOTAL SECULAR

EQUATION. Subroutine MATRIX calls TXFORM and TRANS to prepare the spatial one-electron integrals in final form.

The spatial integrals and the spin matrices are combined to make the secular equation

$$\sum_P U(P) [H(P) - ES(P)] = 0$$

storing $\underline{H}(P)$ and $\underline{S}(P)$ as row vectors of dimension $1/2 \text{ NMAT} \cdot (\text{NMAT}+1)$, where NMAT is $NCON \times ND$.

The routine makes one pass through the spin tape, preparing all contributions of a particular permutation matrix to each matrix element in H and S before reading the next set on IPER and UMAT from the tape.

The function TRX is used to look up the proper two-electron integral and apply any transformations to it, plus doing the p integration. It is called with the indices i,j,k,l and returns the integral $(ij|1/r_{12}|kl)$.

After the secular equation is complete, it is unpacked and stored as two full matrices, HAM and OVP, for use by the diagonalization and search routines.

In the homonuclear case, if the full molecular inversion option has been selected, the secular equation is pretransformed at this

point into block diagonal form, with two blocks of equal size. The block corresponding to the desired symmetry (g or u) will be in the upper left, and only this block will be carried over into the next branch.

Input Deck Setup

The input deck is divided into three sections:

1. Points and weights for numerical quadrature (SETUP branch)
2. Spin information (SETUP branch)
3. Problem definition and electron information (MAIN branch)

Section 1 is common to all calculations in which a specific quadrature rule is desired, and is retained in memory intact throughout the entire run. Section 2 is common to all calculations involving the same number of electrons and a specific spin multiplet. It is used to produce the spin tape, which is retained until subsequent data cards redefine the spin problem. Section 3 is only common to the calculation which is immediately in progress.

One comment is necessary here. This program was designed to be compatible with any machine which accepts a FORTRAN IV language. Due to differences from system to system, all input-output statements involving tapes (common input tape, work tapes, etc.) use symbolic names. The actual numbers can be read from data cards, with one important exception. The symbolic tag of the common input tape for a particular system must be set internally. Therefore, even though this is not part of the input deck, this is included here. In the main program, the variable IN must be set to correspond to the logical tape

number for the system common input tape. (Example - for the Honeywell Automath 800/1800, IN = 2, for IBM 7094/7044 DCOS, IN = 5).

The setup for the input deck proper is as follows:

<u>BRANCH</u>	<u>CARD NO.</u>	<u>FORMAT</u>	<u>LIST</u>
<u>SETUP</u>	<u>1</u>	<u>(12I3)</u>	<u>KW, KR, NT, KINT, IOUT, NPCH</u>

KW - Write tape for integral tables

KR - Read tape for integral tables

NT - Spin tape

KINT - Two electron integral tape

IOUT - Logical number of system common output tape

NPCH - Logical number of system common punch tape

<u>SETUP</u>	<u>2</u>	<u>(6X, 2F8, E30.12, 2A6)</u>	<u>JMAX, NMINUS, WTINF, RULE</u>
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JMAX - Number of points in quadrature formula

NMINUS - Number of points to be accumulated negatively
(See WT below)

WTINF - Weight of point at infinity (= 0 for Gaussian quadratures)

RULE - Alphabetic name of quadrature formula (limited to 12 letters)

<u>SETUP</u>	<u>3-12</u>	<u>(6X, 4E18.12)</u>	<u>POINT</u>
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POINT - Array of quadrature points (Maximum = 40 points)

<u>SETUP</u>	<u>13-22</u>	<u>(6X, 4E18.12)</u>	<u>WT</u>
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WT - Array of weights corresponding to points. These contain the square root of the weight given by the quadrature formula. Since some may be negative leading to imaginary roots, only absolute values are stored, with the first MINUS weights being the negative ones.

<u>SETUP</u>	<u>1</u>	<u>(12I3)</u>	<u>JNT, NEL, NISP, MULT, ND, IOSH, JGEN</u>
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JNT - Tag. JNT=0, make new spin tape; JNT=1, spin tape already mounted

NEL - Number of electrons

NISP - Number of spin product functions (eigenvalues of S_z)

<u>BRANCH</u>	<u>CARD NO.</u>	<u>FORMAT</u>	<u>LIST</u>
MULT - Spin multiplicity $2S+1$ ND - Number of eigenfunctions of S^2 (= dimension of a one-configuration block of the total secular equation) IOSH - Number of open-shell electrons (See App. I and II) JGEN - Number of hand-generated permutations (See App. I and II)			
<u>SETUP</u>	<u>2(deck)</u>	<u>(14I5)</u>	<u>ISP</u>
ISP - Spin product functions. Read as column vector of dimension NISP			
<u>SETUP</u>	<u>3(deck)</u>	<u>(5F14.10)</u>	<u>USET</u>
USET - Coefficient matrix for eigenfunctions of S^2. Dimension $ND \times NISP$, read as column vectors.			
<u>SETUP</u>	<u>4(deck)</u>	<u>(F9.4,21I3)</u>	<u>SIG,JPRI,KPRI</u>
SIG - Parity of a hand-generated permutation JPRI - Hand-generated permutation (Example - +1. 3 4 1 2) KPRI - Aux. permutation with double occupancies noted Note - if JNT = 1, card decks 2, 3, and 4 are omitted.			
<u>MAIN</u>	<u>1</u>	<u>(8A6,3F10.6)</u>	<u>TITLE,A1,A2,EFIN</u>
TITLE - Run identification of 48 characters, to be printed on each output page A1 - Atomic energy of atom 1 A2 - Atomic energy of atom 2 (A1,A2 used to calculate dissociation energy) EFIN - Experimental energy. If $E_{calc} < E_{fin}$, the program assumes an error exists and stops. If no error test is desired, set EFIN = 0.			
<u>MAIN</u>	<u>2</u>	<u>(7F10.4)</u>	<u>ZA,ZB,RMAX,STEP3,STEP2,RMIN,RSTEP</u>
ZA - Nuclear charge of atom A ZB - Nuclear charge of atom B RMAX - Maximum internuclear separation. STEP3 - Maximum step size in variation of non-linear parameters STEP2 - Minimum step size in variation of non-linear parameters			

<u>BRANCH</u>	<u>CARD NO.</u>	<u>FORMAT</u>	<u>LIST</u>
			RMIN - Minimum internuclear separation. If blank, only RMAX is used. RSTEP - Decrement to RMAX until $R \leq RMIN$
<u>MAIN</u>	<u>3</u>	<u>(12I3)</u>	<u>N,NHUG,NCON,NFCN,NPC,NE,LSRCH,NOTRF,NU,KOLD,IS</u>
			N - Number of electrons (used as check on NEL and spin tape) . NHUG - Tag. 0 = Heteronuclear; ± 1 = Homonuclear with symmetrized orbitals; ± 2 = Homonuclear with inversion of total molecule; > 0 = gerade, < 0 = ungerade. NCON - Number of spatial configurations NFCN - Number of spatial functions NPC - Number of functions whose parameters are to be varied. For single calculation, set = 0. NE - Eigenvalue to be minimized. 0 = ground state, 1 = 1st excited state, etc. LSRCH - Search tag. 0 = standard step and gradient search. > 0 = linear search of LSRCH steps in positive direction. NOTRF - Spatial transformation tag. < 0, read C_{ij} from cards; = 0, no transformation; = 1, project out first NU functions from specified orbitals; = 2, orthonormalize all spatial functions. NU - See NOTRF. If NOTRF = 0, NU can be used to start parameter search in NU + 1st spatial function. KOLD - Variation tag. = 0, vary each spatial function independently; = 1, vary i and i + NFCN/2 simultaneously. IS - Search tag. 0 = search α as $3/2 \alpha$, α, $1/2 \alpha$, ≥ 2 search α as δ. (Special note: if an old integral tape KR exists, IS = 2 will set ITX = 2. This provides a convenient restart if the last KW tape has been saved.)
<u>MAIN</u>	<u>4(deck)</u>	<u>(I5,2F10.6,6I3)</u>	<u>I,FPAR(1,I),FPAR(2,I),(NFPAR(J,I),J=1,6)</u>

Spatial function cards

I - Function number

FPAR(1,I) - δ_i

FPAR(2,I) - α_i

NFPAR(1,I) - n_i

<u>BRANCH</u>	<u>CARD NO.</u>	<u>FORMAT</u>	<u>LIST</u>
	NFPAR(2,I)	- m_i	
	NFPAR(3,I)	- v_i	
	NFPAR(4,I)	- Parity of symmetrized orbital 0 = gerade, + 1 = ungerade	
	NFPAR(5,I)	- Projection tag. = 0 - no projection; = 1, project out 1 st NU functions	
	NFPAR(6,I)	- Variation tag. = 0, search both δ and α ; = 1, search α only; = 2, search δ only; = 3, no search of this function	
<u>MAIN</u>	<u>5(deck)</u>	<u>(12I3)</u>	<u>I, (LCON(I,J), J=1,N)</u>
	I - configuration number		
	LCON - Array of function numbers belonging to the configurations		
<u>MAIN</u>	<u>6(deck)</u>	<u>(6E12.7)</u>	<u>((C(I,J), J=1,N), I=1,N)</u>
	C - Transformation matrix for spatial functions. No deck unless NOTRF = -1		

APPENDIX III. ILLUSTRATIVE EXAMPLES

AND HINTS - THE NO^+ CALCULATION

Illustrative examples are furnished to allow the reader to see just how an input deck is set up for a particular type of problem, and as calculations which can be used to check that the program is running properly on a particular computer after the minor modifications necessary to make it compatible with that computer have been made.

Three problems are listed in the sample input decks of Table . The first of these is a LiH calculation, illustrating the heteronuclear capability of the program. This is a one-configuration four electron singlet calculation, and the correct results for the lowest root are:

1. Total electronic energy = -9.708228 au
2. Electronic + nuclear (potential curve) = -7.708228 au
3. Dissociation energy = -7.708228 au

The input deck for this run is self-explanatory once the summary in Appendix II is understood.

The second example is an H_2 calculation using the symmetrized one electron orbitals and two configurations, $C_1 \sigma_g \text{ls} \sigma_g \text{ls}' + C_2 \sigma_u \text{ls} \sigma_u \text{ls}'$. This is for the ground state and the calculated energies should be:

1. Total electronic energy = -1.869461 au
2. Electronic + nuclear (potential curve) = -1.155176 au
3. Dissociation energy = - .155176 au

Note that NHUG = +1 for a gerade state with symmetrized orbitals.

Third, the H_2 calculation is repeated using the option of total inversion of the molecule through the inversion center, selecting the gerade linear combination $\Psi + i\Psi$. Several things should be noted here. The first is that the reflected counterpart of each function (same function with α replaced by $-\alpha$) is included explicitly in the input deck, and that all unreflected functions precede the reflected ones so that if there are m unreflected functions $1, 2, \dots, m$, and each corresponding reflected function is denoted $1', 2', \dots, m'$, the input functions are numbered $1, 2, \dots, m, m+1 = 1', m+2 = 2', \dots, m+m = m'$. The configuration cards are treated similarly, in that each configuration cards are treated similarly, in that each configuration made of unreflected orbitals must be paired with a configuration composed of the corresponding reflected orbitals, with all unreflected configurations. The program combines the reflected configurations with a rotation by π and adds or subtracts the paired configurations as necessary for g or u. Note that NFCN and NCON are set for the total number of functions and configurations. NHUG = +2 is the tag which instructs the program to perform the rotation and block diagonalize the total secular equation taking only the g block.

The energies in this case are:

1. Total electronic energy = -1.791067 au
2. Electronic + nuclear (potential curve) = -1.076781 au
3. Dissociation energy = -.076781 au

Note that although the same functions were used in both H_2 calculations, the one with symmetrized orbitals has a slightly lower energy. This is because the symmetrized orbitals allow two linear coefficients, while in the total molecular inversion option there is only one. The total inversion, in effect, gives $C'_1(\sigma\sigma+\sigma'\sigma') = C_1(\sigma_g\sigma_g+\sigma_u\sigma_u)$, and we see that $C_1 = \sqrt{2}/2$. However, the total inversion requires only 3/2 to 3/4 the work required by the symmetrized orbitals, and if only $\sigma_g\sigma_g$ were used in the symmetrized case, a poorer answer would result.

The $C_1\sigma_g\sigma_g + C_2\sigma_u\sigma_u$ calculation can be improved by varying the parameters of the σ_u orbitals, since they are not restricted to be equal to the parameters of the σ_g orbitals as is the case of total inversion. They were set equal purely to demonstrate the relative effect of the two options.

Some specific hints are also helpful for actual use of the program on particular computers.

On machines having some type of CHAINing feature, the programs themselves can be overlaid. For example, the IBM 7094/7044 DCOS IBSYS monitor, version 13, was used with three links. The INTEGRAL, MATRIX, and SEARCH branches were included in one link for optimum efficiency, and the SETUP and OUTPUT branches formed the other two links.

An additional space-speed saving can be effected in systems with adjustable input-output buffer sizes, such as the Honeywell Automath 800/1800 monitor, by buffering the two-electron integral tape to the smallest possible size, since only two words are written per logical record; and by buffering the spin-permutation tape to the smallest size which will include $N + ND \times ND$ words in one logical record. Tapes KW and KR should be buffered with the largest double buffers possible, since tape handling by subroutine INTEG is the time-controlling factor.

On the Honeywell 800/1800 system, a small calling program is necessary to set up the monitor for use with variable tape identifiers. The entire deck setup is as follows:

```
*JOBID,JOBNAME,IO020305,08SN0025,09DB0019,06DB0200,07DB0200
* Project number xxx, users name, any special instructions to
* be typed at console for operator. (64 columns/card)

TITLEMOLEC
  CALL DIAT
  I=0
  WRITE(6)I
  WRITE(7)I
  WRITE(8)I
  WRITE(9)I
  END
TITLEDIAT --- entire diatomic program deck as presented in App. IV
*DATA
  6 7 8 9 3 5 (Tape identifiers, corresponding to *JOBID card
                above)
-Remainder of input deck-
999
*ENDFILE
```

On the other hand, when the IBM 7094/7044 DCOS system is used, the monitor sets up all buffers when variable tape names are used, and

rather than tricking the monitor with the four statements `WRITE(n)I` above, one must use a MAP program which deletes the unused buffers. Copies of this program are available on request, or the following logic may be used to create the program for a specific installation. To delete the buffer for peripheral unit `nu`, the MAP program is

```
$IBMAP BUF.      NODECK
      ENTRY      .UNnn.
.UNnn. PZE
      END
```

The `ENTRY` and `PZE` instructions are repeated with different numbers $\phi 1$, $\phi 2$, ... as desired to delete any unnecessary unit.

The format for control cards, accounting cards, etc. can be found by consulting the appropriate IBM manuals and the notices published by the particular installation.

In the program listings (App. IV) the reader will note several comment cards relevant to particular machines, and accompanying FORTRAN statements. These must be included or pulled as necessary. The comments are considered self-explanatory.

The NO^+ Calculation

As an illustration of the use of the spin-permutation program options, the following sample calculation on NO^+ is presented. The approximations used were picked more to illustrate the use of the program than for their physical validity and thus the calculation is by no means a definitive one.

To do a complete 14 electron spin problem, $14! \ 429 \times 429$ matrices $U(P)$ would be required, which is patently impossible. The approxi-

mations used to reduce this number to a manageable one are:

1. The closing of the shells which include the ten inner electrons so that the spatial configuration is approximately represented by

$$\pi 2p_{+N} \pi 2p_{+O} \pi 2p_{-N} \pi 2p_{-O} (\sigma 1s)_N^2 (\sigma 1s)_O^2 (\sigma 2s)_N^2 (\sigma 2s)_O^2 (\sigma 2p_o)_{ON}^2$$

and thus requires only two spin functions

$$\theta_{001}^4 [1/\sqrt{2}(\alpha\beta - \beta\alpha)]^5 \text{ and } \theta_{002}^4 [1/\sqrt{2}(\alpha\beta - \beta\alpha)]^5.$$

2. Orthogonalization of the closed shell (doubly occupied) orbitals. This results in a spatial configuration of seven shells of two-electron pairs which are pairwise orthogonal.

With the open shell electrons listed first, the auxiliary permutation vector for the identity permutation is

$$1 \ 2 \ 3 \ 4 \ 55 \ 66 \ 77 \ 88 \ 99$$

and obviously no permutations are necessary between electrons 55, 66, etc. which reduces the number of permutations necessary for spin reasons to $14!/2^5$. We now take advantage of the spatial orthogonalities which were purposely introduced.

As pointed out in App. I, any permutation which produces three or more integrals $(i|j)$ which are zero can be eliminated, since it cannot contribute to the secular equation. Inspection of the auxiliary permutation vector above shows that only 20 permutations among the first four orbitals can contribute to the secular equation, and that no more than one interchange of the closed shell functions is allowed at a time.

Thus, there are 31 allowed interchanges of the closed shell orbitals with themselves or with the open shell orbitals 1-4.

The twenty allowed permutations of the open shell set result in 620 permutations which can contribute to the secular equation within this particular closed shell and orthogonality system, and the result is 620 2×2 matrices $U(P)$ which is obviously a considerable improvement over the complete open shell treatment.

To make the input deck slightly easier to prepare, the orthogonalities in the set of four open shell electrons are ignored, and all $4!$ permutations among them are produced in the program. Hence there are $31 \times 4! = 744$ permutations and their corresponding $U(P)$ produced.

The input deck for this calculation is shown in Table 11. Note that the paired orbitals are replaced by their canonical numbers, and that $IOSH = 4$. Since the permutations among the ten closed shell electrons are explicitly done by hand, no auxiliary permutation vector is needed in the input deck. The tape identifiers and quadrature points have been omitted. Preparation of the spin tape required about two hours on the Honeywell 800 and about eight minutes on an IBM 7094/7044 direct coupled system.

Once the spin tape was prepared, the NO^+ calculation itself took about three minutes on the 7094 and about twenty minutes on the H-800. The resulting energy was -105.93 au, which is of the right order of magnitude, but does not even show binding over the separated atom calculations of Clementi (1964). Due to limited time available

TABLE 10
SAMPLE INPUT DECK

```

*DATA
  6 7 8 9 3 5
      32
      GAUSSIAN
.190783685503F 01 .174753079771F 01 .161383070701E 01 .150164963465E 01
.140711169265F 01 .132722816436F 01 .125967131766E 01 .120261380877E 01
.115461300423E 01 .111452664241F 01 .108145075383E 01 .105467367377E 01
.103364190379F 01 .101793486429F 01 .100724637642F 01 .100136994325E 01
.730957239412F 03 .139000007231F 03 .567573218103E 02 .307248338223E 02
.192903384927F 02 .132773572106E 02 .973159274421E 01 .746776126583E 01
.593549776333F 01 .485102216521E 01 .405597167027E 01 .345632836893E 01
.299342316015E 01 .262911367674F 01 .233773752605E 01 .210151950149E 01
.000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
.000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
.257983042030E 00 .266649570536E 00 .275984138460E 00 .286203763088E 00
.297570455864F 00 .310412608788F 00 .325157698614E 00 .342384529758E 00
.362910948974F 00 .387950049687F 00 .419409197727E 00 .460517871740E 00
.517319815321F 00 .602908470418E 00 .753376991183E 00 .113289624202E 01
.592394427105F-01 .902087498271F-01 .112694165954E 00 .130977494017E 00
.146545764546F 00 .160138998352F 00 .172206801722F 00 .183062928959F 00
.172949871710F 00 .202069518183F 00 .210599104372F 00 .218700280051E 00
.226524883669F 00 .234219238443E 00 .241927970606F 00 .249797978606E 00
.000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
.000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
      4 6 1 2 4 1
12 10 6 9 5 3
.5773502692 -.2886751346 -.2886751346 -.2886751346 -.2886751346
.5773502692
.0000000000 .5000000000 -.5000000000 -.5000000000 .5000000000
.0000000000
1. 1 2 3 4
LIH TEST RUN
2. 1. 1.5
4 0 1 4
1 2.44 2.53
2 1.60 1.45
3 .92 -.90
4 .64 -.32 1
1 1 2 3 4
2 2 1 1 2 1
1 2
.7071067812 -.7071067812
1.0 1 2
H2 GROUND STATE TEST RUN NO. 1 -1.
1. 1. 1.4
2 1 2 4
1 1.06 .65
2 .65 .67
3 1.06 .65 1
4 .65 .67 1
1 1 2
2 3 4
1 2 2 1 1 2 1
H2 GROUND STATE TEST RUN NO. 2 -1.
1. 1. 1.4
2 2 2 4
1 1.06 .65
2 .65 .67
3 1.06 -.65
4 .65 -.67
1 1 2
2 3 4
999
*ENDFILE

```


TABLE 11

INPUT DECK FOR NO⁺ CALCULATION

[illegible]

to the author, no attempt was made to improve this calculation by variation of the non-linear parameters or by making more realistic physical approximations. Upon completion of the single one-shot run it was decided that the original purpose of this study had been achieved, that of demonstrating that a calculation on a large many-electron diatomic molecule is possible and practical with the present modification of the diatomic program.

The short time required for the actual calculation shows that parameter variation and even some configuration mixing are possible in reasonable amounts of computer time, and a much improved energy obtainable even with the limited spin set used.

APPENDIX IV

LISTING OF DIATOMIC PROGRAM

```

**      ***      ***      ***      ***      ***      ***      ***
** TITLEDJAT
C
C REVISED DIATOMIC MOLECULE PROGRAM
C
C REV. DATE 6/16/66
C
C DATA INPUT AND CONTROL LINK
C INPUT DEFINITIONS
C ZA = CHARGE ON ATOM A
C ZB = CHARGE ON ATOM B
C RMAX = INTERNUCLEAR SEPARATION
C STEP3 = INITIAL STEP SIZE FOR PARAMETER SEARCH
C STEP2 = FINAL TOLERANCE
C RMIN = MINIMUM INTERNUCLEAR SEPARATION
C RSTEP = DECREMENT TO R UNTIL REACHES RMIN
C N = NO. OF ELECTRONS
C NHUG = HET-HOMO-GERADE-UNGERADE TAG. (0=HET,1=UNG,2=GER.)
C NCON = NO. OF SPATIAL CONFIGURATIONS
C NFCN = NO. OF ONE-ELECTRON SPATIAL ORBITALS
C NPC = NO. OF FUNCTIONS(ORBITALS) TO BE VARIED(PARAM, SRCH)
C NE= DESIRED ROOT OF SEC. EQN. (0=GND.STATE, 1=1ST EXCITED ST., ETC)
C LSRCH = LINEAR VS. STEEPEST DESCENT PARAM SRC(0= GRAD,1=LIN.)
C NOTRF = TRANSFORMATION TAG. SEE SUBROUTINE TXFORM
C NU = NUMBER OF FUNCTIONS TO BE PROJECTED OUT IF NOTRF=1 PARAM
C SEARCH STARTS ON NU + 1 ST FUNCTION
** 10 DIA
** 20 DIA
** 30 DIA
** 40 DIA
** 50 DIA
** 60 DIA
** 70 DIA
** 80 DIA
** 90 DIA
** 100 DIA
** 110 DIA
** 120 DIA
** 130 DIA
** 140 DIA
** 150 DIA
** 160 DIA
** 170 DIA
** 180 DIA
** 190 DIA
** 200 DIA
** 210 DIA
** 220 DIA
** 230 DIA
** 240 DIA
** 250 DIA

```



```

C      KSIM = (ITAG(4)) SIMULTANEOUS VARIATION TAG. IF NON-ZERO, VARIES DIA 260
C      MONTH AND NFCN/2-MO-TH FUNCTIONS SIMULTANEOUSLY DIA 270
C      IS = IF #2 , TAPE KR IS MOUNTED FROM PREVIOUS RUN, AND PROG. DIA 280
C      SETS ITX#2 DIA 290
C      FUNCTION CARDS ----- DIA 300
C      DELTA(I)=FPAR(1,I) , ALPHA(I)=FPAR(2,I) DIA 310
C      FPAR# WORKING SET OF DELTA,ALPHA DIA 320
C      FPARO# BEST SET DETERMINED SO FAR DIA 330
C      NFPAR# FIXED EXPONENTS DIA 340
C      N(I)=NFPAR(1,I),M(I)=NFPAR(2,I),NU(I)=NFPAR(3,I),PARITY(I)= DIA 350
C      NFPAR(4,I)(I=U,O=G),NFPAR(5,I)-NOT USED,NFPAR(6,I)-VARIATION TAG DIA 360
C      O#VARY DELT AND ALF,I#VARY ALF ONLY,2#VARY DELT ONLY,3#SKIP BOTH DIA 370
C      CONFIGURATION CARDS ARE READ BY SUBROUTINE CONFIG DIA 380
C      DIMENSION OF H1,S1,H2 BASED ON 16 FUNCTIONS (NFCN=16) DIA 390
C      DIA 400
C      DIA 410
C      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE, DIA 420
C      1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,DIA 430
C      2LSRCH,JKW3,LJAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2) DIA 440
C      3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG( 6),ICTAG(64), DIA 450
C      4DELT(25),HMAX,RMIN,RSTEP,STEP3 DIA 460
C      COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40), DIA 470
C      1WT(40),NMINUS,RULE(2) DIA 480
C      COMMON/WORK/NEL,NISP,MULT1,ND1,IOSH,JGEN,IDEN(3),KW1,KR1,NT1,KOR1,DIA 490
C      1DA(2917) , S1(9588) DIA 500
C      COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9) DIA 510
C      EQUIVALENCE(KR1,I),(KOR1,J) ,(10,LSPARE) DIA 520
C      EQUIVALENCE (ITAG(1),IN),(ITAG(2),KINT) DIA 530
C      EQUIVALENCE (NPCH,ITAG(3)) DIA 540
C      COMMON LCON (150) DIA 550
C      100 FORMAT(12I3) DIA 560
C      101 FORMAT(8A6,3F10.6) DIA 570
C      102 FORMAT(7F10.4) DIA 580
C      103 FORMAT(15,2F10.6,6I3) DIA 590
C      104 FORMAT(1H020X,15HSEC EQN TOO BIGI6) DIA 600

```



```

105 FORMAT(1H020X,15HWRONG PERM TAPE2I6)
111 FORMAT(8E10.5)
C
C HONEYWELL
C IN=2
C FOR IBM SET IN = 5
C MSPARE=42
C ITX=1313
C LIAR=0
C
26 CALL SETUP(IN)
25 REWIND NT
REWIND KW
REWIND KR
READ(IN,101) (SAVEA(I),I=1,8), A1,A2,EFIN
READ(IN,102) ZA,ZB,RMAX,STEP3,STEP2,RMIN,RSTEP
IF(RMIN.EQ.0.)RMIN=RMAX
READ(IN,100) N,NHUG,NCON,NFCN,NPC,NE,LSRCH,NOTRF,NU,ITAG(4) ,IS
IF(IS.EQ.0) IS=1
DO 3 N10=1,NFCN
READ(IN,103) N1,FPARO(1,N1),FPARO(2,N1),(NFPAR(JNT,N1),JNT=1,6)
MO=N1
IF(ABS(FPARO(2,MO)).GT.1.2*FPARO(1,MO)) FPARO(2,MO)=SIGN(1.2*
*FPARO(1,MO),FPARO(2,MO))
FPAR(1,N1)=FPARO(1,N1)
FPAR(2,N1)=FPARO(2,N1)
3 CONTINUE
CALL CONFIG (1,LCON ,N,NCON,IN,IO)
JCODE=1000*N+10*IOSH+MULT
IF(NOTRF.GE.0) GO TO 9
49 DO 48 I=1,N
48 READ(IN,111) (C(I,J),J=1,N)
9 REWIND NT
READ(NT) IDEN
IF(JCODE.NE.IDEN(3)) GO TO 8
DIA 610
DIA 620
DIA 630
DIA 640
DIA 650
DIA 660
DIA 670
DIA 680
DIA 690
DIA 700
DIA 710
DIA 720
DIA 730
DIA 740
DIA 750
DIA 760
DIA 770
DIA 780
DIA 790
DIA 800
DIA 810
DIA 820
DIA 830
DIA 840
DIA 850
DIA 860
DIA 870
DIA 880
DIA 890
DIA 900
DIA 910
DIA 920
DIA 930
DIA 940
DIA 950

```



```

REWIND NT
ND=IDEN(1)
MMAT=NFCN*(NFCN+1)/2
NMAT=NCON*ND
IF(NMAT.GT.MSPARE) GO TO 10
IF(NPC.NE.0) NPC=NPC+NU
IF(IABS(NHUG).EQ.2) ITAG(4)=1
5 R=RMAX
MO = 1 + NU
NO=1
ITX=1
IF(15.EQ.2) ITX=2
STEP1 = STEP3
11 CALL HDG
CALL CONFIG (2,LCON ,N,NCON,IN,10)
7 CALL INTEG
CALL MATRIX( IN,LCON ,NCON,N)
CALL SEARCH
IF(ITX.NE.0) GO TO 7
CALL OUTPUT (LCON ,NCON,N)
IF(RMAX.LE.RMIN) GO TO 1
RMAX=RMAX-RSTEP
R=RMAX/R
DO 22 I=1,2
DO 22 J=1,16
FPARO(I,J)=FPARO(I,J)*R
22 FPAR(I,J)=FPARO(I,J)
GO TO 5
8 WRITE(10,105) JCODE, IDEN(3)
CALL EXIT
10 WRITE(10,104) NMAT
CALL EXIT
1 CALL SSWTCH(4,MORE)
IF(MORE.NE.1) GO TO 222
REWIND NPCH
DIA 960
DIA 970
DIA 980
DIA 990
DIA 1000
DIA 1010
DIA 1020
DIA 1030
DIA 1040
DIA 1050
DIA 1060
DIA 1070
DIA 1080
DIA 1090
DIA 1100
DIA 1110
DIA 1120
DIA 1130
DIA 1140
DIA 1150
DIA 1160
DIA 1170
DIA 1180
DIA 1190
DIA 1200
DIA 1210
DIA 1220
DIA 1230
DIA 1240
DIA 1250
DIA 1260
DIA 1270
DIA 1280
DIA 1290
DIA 1300

```



```

WRITE(NPCH,101) (SAVEA(I),I=1,8),A1,A2,EFIN
WRITE(NPCH,102) Z,ZB,R,STEP3,STEP2,RMIN,RSTEP
MU=NFCN-MO -1
WRITE(NPCH,100) N,NHUG,NCON,NFCN,MU,NE,LSRCH,NOTRF,MO
DO 333 NI=1,NFCN
333 WRITE(NPCH,103) NI,FPARO(1,N1),FPARO(2,N1),(NFPAR(JNT,N1),JNT=1,6)DIA 1310
CALL CONFIG(3,LCON ,N,NCON,IN,NPCH) DIA 1320
ENDFILE NPCH DIA 1330
222 READ(IN,100) JNT,NEL,NISP,MULT,ND,IOSH,JGEN DIA 1340
IF(JNT.EQ.999) CALL EXIT DIA 1350
C HONEYWELL 800 ONLY - FOR SOME REASON THIS PREVENTS UNDEFINED DIA 1360
C TAPE POSITION ERRORS WHEN STARTING A NEW CALCULATION. DIA 1370
C KW=6 DIA 1380
C KR=7 DIA 1390
C IF(JNT.NE.O) GO TO 25 DIA 1400
C GO TO 26 DIA 1410
C END DIA 1420
*** ***** ***** ***** ***** ***** ***** ***** **
SUBROUTINE HDG
PRINTS HEADING LINES IN OUTPUT
COMMON/SPACE/ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARSE,MSPARE,ITX,N1,NC1,NC2P,
2LSRCH,JKW3,LIAR,STEP1,STEP2,EQ,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)HDG
3 ,FPARU(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8), HDG
4DELT(25),KMAX,RMIN,RSTEP,STEP3 HDG
COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40), HDG
1WT(40),NMINUS,RULE(2) HDG
EQUIVALENCE(I,JNT),(TUP,NC2P)
EQUIVALENCE (IO,LSPARSE)
EQUIVALENCE (BLANK,ICTAG)
DIMENSION MAG(8),BLANK(3)
DATA(MAG(1),J=1,8)/5HHETER,5H HOM,5HONUC.,5H GER ,5H UNG ,5HMOL,HDG
999

```



```

* I,6HNVERTD,6H /
10 FORMAT(15X,12HCJT W SSWTCH /)
303 FORMAT(1H18A6//7X,3HZA=F8.2,3X,3HZB=F8.2,3X,2HN=I2,3X,5H2S+1=I2,3XHDG
* ,2HC=I2,3X,2HR=F8.3,4H(AU)3X,2HR=F8.4,5H(ANG) /)
TUP3 .52917*R
WRITE(10,303)(SAVEA(1),I=1,8),ZA,ZB,N,MULT,NCON,R,TUP
100 FORMAT(15X,3A5,2A6 /)
IF(NHUG.EQ.0) GO TO 2
BLANK(1)=HAG(8)
BLANK(2)=HAG(8)
IF(IABS(NHUG).NE.2) GO TO 3
BLANK(1)=HAG(6)
BLANK(2)=HAG(7)
BLANK(3)=HAG(4)
3 IF(NHUG.LT.0) BLANK(3)=HAG(5)
WRITE(10,100) HAG(2),HAG(3),BLANK(3),BLANK(1),BLANK(2)
GO TO 7
2 WRITE(10,100) HAG(1),HAG(3)
7 CONTINUE
IF(LIAR.NE.0) WRITE(10,10)
WRITE(10,107) RULE,JMAX
107 FORMAT(1H0,20X,2A6,21HINTEGRATION, NO. PTS= I4 /)
9 RETURN
END
HDG 150
HDG 160
HDG 170
HDG 180
HDG 190
HDG 200
HDG 210
HDG 220
HDG 230
HDG 240
HDG 250
HDG 260
HDG 270
HDG 280
HDG 290
HDG 300
HDG 310
HDG 320
HDG 330
HDG 340
HDG 350
HDG 360
HDG 370
HDG 380

```



```

C      SUBROUTINE CONFIG( NRW,LCON,N,NCON,IN,IO)
C      READ OR PRINT CONFIG CARDS
C      DIMENSION LCON(NCON,N)
100  FORMAT(12I3)
106  FORMAT(5X,4HCONF,17,5X,3HFCN 2X,20I3)
      GO TO (1,2,3),NRW
1    DO 4 N10= 1,NCON
      READ(IN,100) N1,(LCON(N1,JNT),JNT=1,N)
4    CONTINUE
      RETURN
2    DO 20 N1=1,NCON
20   WRITE(IO,106)N1,(LCON(N1,J),J=1,N)
      RETURN
3    DO 21 N1=1,NCON
21   WRITE(IO,100)N1,(LCON(N1,J),J=1,N)
      RETURN
      END
CON 10
CON 20
CON 30
CON 40
CON 50
CON 60
CON 70
CON 80
CON 90
CON 100
CON 110
CON 120
CON 130
CON 140
CON 150
CON 160
CON 170

```

```

**      ***      ***      ***      ***      ***      ***      ***
**      SUBROUTINE SETUP (IN)
C      CONTROLLING PROGRAM OF SETUP      BRANCH
C      SETS PERMANENT DATA BLOCK AND MAKES INITIAL SPIN TAPE
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
INPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,SET
2LSRCH,JKW3,LJAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)SET
3  ,FPARU(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),SET
4DELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/WORK/NEL,NISP,MULT1,ND1,IOSH,JGEN,IDEN(3),KW1,KR1,NT1,KOR1,SET
1DA(2917)  , S1(9588)
      EQUIVALENCE (IOUT,LSPARE)
      EQUIVALENCE (ITAG(2),KINT)      ,(ITAG(3),NPCH)
100  FORMAT(12I3)
      IF(ITX,NE,1313) GO TO 1
      READ(IN,100) KW,KR,NT,KINT, IOUT,NPCH
      CALL TABLE(IN)
      READ(IN,100) JNT,NEL,NISP,MULT,ND,IOSH,JGEN
1    IF(JNT.EQ.0) CALL SPIN (NT,NPERMS,IN,NEL,NISP,MULT,ND,IOSH,JGEN,
SET 10
SET 20
SET 30
SET 40
SET 50
SET 60
SET 70
SET 80
SET 90
SET 100
SET 110
SET 120
SET 130
SET 140
SET 150
SET 160
SET 170
SET 180

```



```

1 IDEN,DA(1),DA(785),DA(857),DA(1577),DA(1600),DA(1650),S1)
RETURN
END

**      ***      ****      ****      ****      ****      ****      ****
SUBROUTINE TABLE (M)
  MAKES PERMANENT DATA BLOCK FOR INTEGRAL ROUTINES
  COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
  1 WT(40),NMINUS,RULE(2)
  EQUIVALENCE (WT(1),I),(WT(2),J),(WT(3),K),(WT(4),A),(WT(5),B),
  *(WT(6),C)
  APPENDIX II - EQN (64)
  DO 1 I=1,7
  DO 1 J=1,7
  DD1(I,J)=0.
  DD1(I,1)=1.
  DO 5 I=2,7
  A=2*I-1
  DD1(I,1)=DD1(I-1,I-1)*SQRT(A*(A-1.))
  DO 6 J=1,7
  K=J+1
  DO 6 I=K,36
  A=1+J-2
  B=2*I-1
  C=I-J
  DD1(I,J)=DD1(I-1,J)*SQRT(A/C*B/(B-2.))
  APPENDIX II - EQN (65)
  DO 2 I=1,11
  DO 2 J=1,11
  D1(I,J)=0.
  D1(1,1)=1.
  DO 3 I=2,11
  A=I-1
  B=2*I-3
  D1(I,1)=D1(I-1,I-1)*A/B
  DO 4 J=1,9
  K=J+2

```



```

DO 4 I=K,11,2
  A=I-1
  C=I-J
  B=I+J-1
  4 D1(I,J)=D1(I-2,J)*A/C*(A-1.)/B
C  APPENDIX II - EQN (66)
  DO12 I=1,43
  DO12 J=1,7
    A=I+J-1
    B=I-J+1
    C=4*I*I-1
  12 DD2(I,J)=A*B/C
    READ(M,100) JMAX,NMINUS,WTINF ,RULE
    READ(M,101) PUINT
C  APPENDIX II - EQN (67)
  READ(M,101) WT
  RETURN
  100 FORMAT(6X,2I8,E30,12,2A6)
  101 FORMAT(6X,4E18,12 )
  END

**      ***      ***      ***      ***      ***      ***      ***
SUBROUTINE SPIN (NT,NP,IN,N ,NISP,MULT,ND,IOSH,JGEN,IDEN,UMAT,
*ISP,ITE,ISSPM,JPRI,I1,USET)
C  MAKES PERM TAPE OF UMAT AND IPER WITH OPTIONS RANGING FROM CLOSED
C  SHELL TO COMPLETE OPEN SHELL
C
C  SPACE AND DIMENSIONS ARE SUFFICIENT FOR HANDLING THE  FULL
C  EIGHT ELECTRON PROBLEM
C
  INPUT
  NEL - NUMBER OF ELECTRONS
  NISP - NUMBER OF SIMPLE SPIN PRODUCT FUNCTIONS (AABBA...)
  MULT - MULTIPLICITY (2S+1)
  ND - DEGENERACY (FNS OF KOTANI)
  IOSH - NUMBER OF ELECTRONS TO BE INCLUDED IN PERM. SCAN
  JGEN - NUMBER OF HAND GENERATED PERMUTATIONS

```

TBL 330
TBL 340
TBL 350
TBL 360
TBL 370
TBL 380
TBL 390
TBL 400
TBL 410
TBL 420
TBL 430
TBL 440
TBL 450
TBL 460
TBL 470
TBL 480
TBL 490
TBL 500
TBL 510
TBL 520

** *** *** *** *** *** *** ***
SPN 10
SPN 20
SPN 30
SPN 40
SPN 50
SPN 60
SPN 70
SPN 80
SPN 90
SPN 100
SPN 110
SPN 120
SPN 130
SPN 140
SPN 150


```

C      ( PERMS WHICH PRODUCE ZEROS DUE TO CLOSING OF SHELLS OR SPATIAL
C      ORTHOGONALITIES ARE OMITTED BY PROPER PREPARATION OF JGEN LIST
C
C      INPUT (CARDS)
C      ISP = ACTUAL CODING OF BIT CONFIGURATIONS FOR SPIN PRODUCT FUNCTION
C      USET = COEFFICIENT MATRIX (DIMENSION NDXNISP)
C      JPRI = UNPAIRED TRUE PERMUTATION VECTOR
C      KPRI = AUXILIARY PERM VECTOR WITH PAIRS INDICATED
C
C      OUTPUT = ON TAPE NT
C      UMAT=ANTISYMMETRIZED MATRIX REPRESENTATION OF PERMUTATIONS
C      IPER = THE ACTUAL PERMUTATIONS (PERMUTED FUNCTION NUMBERS)
C      NP = THE NUMBER OF SETS (UMAT,IPER) WRITTEN ON TAPE NT
C
C      DIMENSION IDEN(3),UMAT(ND,ND),ISP(NISP),ITE(NISP,N),ISSPM(N),
C      *JPRI(N),II(N),USET(ND,NISP),KPRI(20)
C      100 FORMAT(14I5)
C      101 FORMAT(5F14.10)
C      102 FORMAT(F9.2,2I3)
C      REWIND NT
C      DO 110 I=1,ND
C      DO 9 J=1,ND
C      9 UMAT(I,J)=0.
C      110 UMAT(I,I)=1.
C      NP=0
C      LOCA=0
C      READ(IN,100) (ISP(I),I=1,NISP)
C      UNPACK ISP INTO ITE
C      DO 11 I=1,NISP
C      IX = ISP(I)
C      IZ = 2*(N-1)
C      DO 11 J=1,N
C      ITE(I,J)=IX/IZ
C      IX=IX-IZ*ITE(I,J)
C      11 IZ = IZ/2

```

SPN 160
 SPN 170
 SPN 180
 SPN 190
 SPN 200
 SPN 210
 SPN 220
 SPN 230
 SPN 240
 SPN 250
 SPN 260
 SPN 270
 SPN 280
 SPN 290
 SPN 300
 SPN 310
 SPN 320
 SPN 330
 SPN 340
 SPN 350
 SPN 360
 SPN 370
 SPN 380
 SPN 390
 SPN 400
 SPN 410
 SPN 420
 SPN 430
 SPN 440
 SPN 450
 SPN 460
 SPN 470
 SPN 480
 SPN 490
 SPN 500


```

DO812 I=1,ND
  READ(IN,101) (USET(I,J),J=1,NISP)
812 USET(I,NISP+1)=0.
  IDEN(1)=ND
  IDEN(2) = N
  IDEN(3)= 1000*N +10*IOSH+MULT
  WRITE(NI) IDEN
  JIPER = 1
20 READ(IN,102) SIG, (JPRI(K), K=1,N) , (KPRI(K),K=1,N)
  IF(KPRI(1).NE.0) GO TO 999
  DO 998 K=1,N
    KPRI(K)=JPRI(K)
998 KPRI(K)=JPRI(K)
999 IF (NP.EQ.0) GO TO 27
  GO TO 116
21 K1=IOSH-1
  DO 301 K=1,K1
    IF(KPRI(K+1).GT.KPRI(K)) GO TO 302
301 CONTINUE
  IF(JIPER.GE.JGEN) GO TO 117
  JIPER = JIPER + 1
  GO TO 20
302 DO 303 L=1,K
  ISSPM(L)=KPRI(L)
303 I1(L)= JPRI(L)
  DO 304 L=1,K
    K1 = K-L+1
    KPRI(L)=ISSPM(K1)
304 JPRI(L) = I1(K1)
  DO 305 L=1,K
    IF(ISSPM(L).LT.KPRI(K+1)) GO TO 306
305 CONTINUE
306 K1 = K-L+1
  JPRI(K1) = JPRI(K+1)
  KPRI(K+1) = I1(L)
  KPRI(K1) = KPRI(K+1)

```

SPN 510
SPN 520
SPN 530
SPN 540
SPN 550
SPN 560
SPN 570
SPN 580
SPN 590
SPN 600
SPN 610
SPN 620
SPN 630
SPN 640
SPN 650
SPN 660
SPN 670
SPN 680
SPN 690
SPN 700
SPN 710
SPN 720
SPN 730
SPN 740
SPN 750
SPN 760
SPN 770
SPN 780
SPN 790
SPN 800
SPN 810
SPN 820
SPN 830
SPN 840
SPN 850


```

      KPRI(K+1)= ISSPM(L)
      IF(MOD(K+4).LT.2) SIG=-SIG
116 DO 10 I=1,NISP
10  ISSPM(I)=0
      DO 14 I=1,NISP
      IX = 0
      DO 12 K=1,N
      IX = 2*IX
      I3=JPRI(K)
12  IX = IX + ITe(I,I3)
      DO 13 K=1,NISP
      IF(IX.NE.ISP(K)) GO TO 13
      ISSPM(K)=I
      GO TO 14
13  CONTINUE
14  CONTINUE
      DO 1180 I=1,ND
      DO 1180 L=1,ND
      UTEM=0
      DO 1175 J = 1,NISP
      K=ISSPM(J)
      IF(K.EQ.0) GO TO 1175
      UTEM=UTEM+USET(I,J)*USET(L,K)
1175 CONTINUE
1180 UMAT(I,L) = UTEM*SIG
27  WRITE(NT) (JPRI(I),I=1,N),((UMAT(K,J),K=1,ND),J=1,ND)
      NP = NP+1
      GO TO 21
117  ENDFILE NT
      REWIND NT
      RETURN
      END

```

SPN 860
 SPN 870
 SPN 880
 SPN 890
 SPN 900
 SPN 910
 SPN 920
 SPN 930
 SPN 940
 SPN 950
 SPN 960
 SPN 970
 SPN 980
 SPN 990
 SPN 1000
 SPN 1010
 SPN 1020
 SPN 1030
 SPN 1040
 SPN 1050
 SPN 1060
 SPN 1070
 SPN 1080
 SPN 1090
 SPN 1100
 SPN 1110
 SPN 1120
 SPN 1130
 SPN 1140
 SPN 1150
 SPN 1160
 SPN 1170


```

C
C SUBROUTINE INIEG
C
C CONTROLLING PROGRAM OF INTEGRAL BRANCH
C GENERATES AND STORES ONE AND TWO ELECTRON INTEGRALS
C KW= WRITE TAPE, KR= READ TAPE WITH BEST SET OF INTEGRALS TO DATE
C JTA AND JTB ARE COMPLETE INTEGRAL TABLES, WITH ALL DATA NECESSARY
C FOR COMBINING TO MAKE THE TWO ELECTRON INTEGRALS./
C
C SEE SUBROUTINE ONEL FOR TABLE LAYOUT OF (JTA(I,L),I=1,1460)
C TOTAL INTEGRAL PACKAGE CONSISTS OF BANDI,GLIST, ONEL, TWOEL
C COMBIN AND TAPE
C
C COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
C 1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,INT
C 2LSRCH,JKW3,LJAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)INT
C 3,FPAR0(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),INT
C 4DELT(25),RMAX,RMIN,RSTEP,STEP3
C COMMON/WORK/JTB(1460,4),JTA(1460,4),I,J,L,L1,NTOT,DUMBO(289)INT
C 1,S1(136),H1(136),REST(272)INT
C COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),INT
C 1WT(40),NMINUS,RULE(2)INT
C COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)INT
C EQUIVALENCE (LSPARE,IO)INT
C EQUIVALENCE (ITAG(2),KINT)INT
C EQUIVALENCE (JTA,ZG1),(JTB,H2)INT
C DIMENSION H2(9317),ZG1(1460,4)INT
C DATA FINAL/6HNOMORE/INT
C
C 303 REWIND KW
C REWIND KINT
C REWIND NT
C REWIND KR
C NTOT=1
C L=0
C L1=0

```



```

DO 302 I=1,NFCN
DO 302 J=1,I
  L1=L1+1
  IX=NFCN/2
  IF(NOTRF.EQ.1) IX=IX+NU
  IF((IABS(NHUG).EQ.2).AND.(J.GT.IX )) GO TO 301
  L=L+1
  IF(ITX.EQ.1) GO TO 309
  IF(L.EQ.1) CALL TAPE(KR,1,JTA)
  IF(JTA(11,L).EQ.L1) GO TO 309
358 WRITE(10,399)L1,JTA(11,L),J,JTA(8,L),J,JTA(9,L)
  CALL EXIT
309 CALL ONEL(I,J,JTA(1,L),JTA(1,L),JMAX)
  JTA(11,L)=L1
  S1(L1)=ZG1(17,L)
  IF(J.NE.I) GO TO 400
  REST(I)=SQRT(S1(L1))
  MERDE=IX+I
  IF(IABS(NHUG).EQ.2) REST(MERDE)=REST(I)
400 H1(L1)=(2.*ZG1(10,L)-ZG1(18,L))/(2.*R))/R
  IF(L.LT.4) GO TO 302
  CALL TAPE(KW,2,JTA)
  L=0
  NTOT=NTOT+1
301 CONTINUE
302 CONTINUE
  L1=L+1
DO 300 I=L1,4
  JTA(11,I)=0
300 JTA(12,I)=20
  CALL TAPE(KW,2,JTA)
  ENDFILE KW
  REWIND KW
  L1=0
  C  NORMALIZE

```

```

INT 360
INT 370
INT 380
INT 390
INT 400
INT 410
INT 420
INT 430
INT 440
INT 450
INT 460
INT 470
INT 480
INT 490
INT 500
INT 510
INT 520
INT 530
INT 540
INT 550
INT 560
INT 570
INT 580
INT 590
INT 600
INT 610
INT 620
INT 630
INT 640
INT 650
INT 660
INT 670
INT 680
INT 690
INT 700

```



```

DO 304 I=1,NFCN
DO 304 J=1,I
  L1=L1+1
  X=REST(I)*REST(J)
  S1(L1)=S1(L1)/X
  H1(L1)=H1(L1)/X
  IF(I.EQ.J) S1(L1)=1.
304 CONTINUE
  I=L+4*(NTOT-1)
  I=I*(I+1)/2 +1
310 CALL COMBIN(JTA,JTB,KINT,R,JMAX,REST)
  IF(NTOT.EQ.1) GO TO 241
  NTOT=NTOT-1
  DO 311 LI=1,NTOT
    IX=1
    CALL TAPE(KW,IX,JTB)
    IF(IX.EQ.13) GO TO 303
    CALL COMBIN(JTA,JTB,KINT,R,JMAX,REST)
311 CONTINUE
    CALL COMBIN(JTB,JTB,KINT,R,JMAX,REST)
    IF(NTOT.EQ.1) GO TO 241
    NTOT=NTOT-1
    DO 312 LI=1,NTOT
      BACKSPACE KW
      BACKSPACE KW
      IX=1
      CALL TAPE(KW,IX,JTA)
      IF(IX.EQ.13) GO TO 303
      CALL COMBIN(JTA,JTB,KINT,R,JMAX,REST)
312 CONTINUE
      GO TO 310
241 WRITE(KINT) I,FINAL
      ENDFILE KINT
242 REWIND KINT

```

INT 710
 INT 720
 INT 730
 INT 740
 INT 750
 INT 760
 INT 770
 INT 780
 INT 790
 INT 800
 INT 810
 INT 820
 INT 830
 INT 840
 INT 850
 INT 860
 INT 870
 INT 880
 INT 890
 INT 900
 INT 910
 INT 920
 INT 930
 INT 940
 INT 950
 INT 960
 INT 970
 INT 980
 INT 990
 INT 1000
 INT 1010
 INT 1020
 INT 1030
 INT 1040
 INT 1050


```

313 REWIND KR
    READ(KINT) L1,H2(L1)
    IF(H2(L1).NE.FINAL) GO TO 313
    REWIND KINT
    RETURN
399 FORMAT(1H020X,18HINDICES DONT CHECK3(4X,2I4))
    END

**      ****      ****      ****      ****      ****      ****
**      SUBROUTINE COMBIN (JTA,JTB,NT,R,JMAX,OVP)
**      CONTROLS COMBINATION OF G(I,K) AND G(J,L)
**      DIMENSION JTA(1460,4),JTB(1460,4)
**      IND2(I,K)=MIN0(I,K)+(MAX0(I,K)*(MAX0(I,K)-1)/2)
**      DO 1 I=1,4
**      IF(JTA(I,I).EQ.0) GO TO 1
**      K=4
**      IF(JTB(I,I).EQ.JTA(I,I)) K=I
**      DO 2 J=1,K
**      IF(JTB(I,J).EQ.0) GO TO 2
**      X=TW0EL(JTA(I,I),JTB(I,J),JTA(20,I),JTB(20,J),JTA(1,I),JTB(1,J),R,COM
**      *JMAX,OVP)
**      L1=IND2(JTA(I,I),JTB(I,I,J))
**      WRITE(NT) L1,X
2    CONTINUE
1    CONTINUE
    RETURN
    END

INT 1060
INT 1070
INT 1080
INT 1090
INT 1100
INT 1110
INT 1120
COM 10
COM 20
COM 30
COM 40
COM 50
COM 60
COM 70
COM 80
COM 90
COM 100
COM 110
COM 120
COM 130
COM 140
COM 150
COM 160
COM 170
COM 180

```



```

10 TAP
20 TAP
30 TAP
40 TAP
50 TAP
60 TAP
70 TAP
80 TAP
90 TAP
100 TAP

SUBROUTINE TAPE(NO,KACT,JT)
PACKS,READS, AND WRITES INTEGRAL TABLES G(I,K)
DIMENSION JT(1460,4)
GO TO (1,2),KACT
1 READ(NO) L,((JT(I,J),I=1,L),J=1,4)
RETURN
2 L=MAXO(JT(12,1),JT(12,2),JT(12,3),JT(12,4))
WRITE(NO)L,((JT(I,J),I=1,L),J=1,4)
RETURN
END

** *** ** ** ** **
SUBROUTINE ONEL(J1,J2,TAB,JTAB,JMAX)
TAB LAYOUT = 1-7 NLP,8-J1,9-J2,10-EPOT,11-IND2,12-NWORDS,
13-16 FLP,17-$,18-EKIN,19-GINY,20-1460 GINT
JTAB=TAB FOR PACKING AND UNPACKING FIXED OR FLOAT WORDS.
COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,ONE
2LSRCH,JKW3,L1AR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)ONE
3,FPARQ(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),ONE
4DELT(25),KMAX,RMIN,RSTEP,STEP3
COMMON/WORK/NLP(7),NOTA(5),FLP(4),S,H1,A(7),B(7),BINT(36,2),C(7,2)ONE
1,DUMM(1326), FL1,C2,C3,C5,C6,C7,KRONEK,EDELT,EZETA,EK1,
2EK2,EK3,EK4,EK2PRI,EK3PRI,I,ZG1(1470), RMDR(9588)
DIMENSION TAB(1460), JTAB(1460)
EQUIVALENCE (EPOT,NOTA(3)),(EKIN,H1)
NOTA(1)=J1
NOTA(2)=J2
NOTA(5)=JTAB(12)
FLP(1)=FPAR(1,J1)+FPAR(1,J2)
FLP(2)=FPAR(1,J1)-FPAR(1,J2)
FLP(3)=FPAR(2,J1)+FPAR(2,J2)
FLP(4)=FPAR(2,J1)-FPAR(2,J2)
IF(ITX.EQ.1) GO TO 31
IF(FLP(1).NE.TAB(13))GO TO 31
IF(FLP(2).NE.TAB(14))GO TO 31
IF(FLP(3).NE.TAB(15))GO TO 31

```



```

IF(FLP(4).NE.TAB(16))GO TO 31
RETURN
31 NLP(1)=NFPAR(3,J1)-NFPAR(3,J2)
   NLP(2)=(IABS(NFPAR(3,J1))+IABS(NFPAR(3,J2))-IABS(NLP(1)))/2
   NLP(3)=NFPAR(2,J1)+NFPAR(2,J2)
C   NLP(4) OR L4 TO BE REDETERMINED BY BANDI IF ENTERED
   NLP(4)=JTAB(4)
   NLP(5)=NFPAR(1,J1)+NFPAR(1,J2)
   NLP(6)=NFPAR(2,J1)-NFPAR(2,J2)
   NLP(7)=NFPAR(1,J1)-NFPAR(1,J2)
   MMM      =NFPAR(2,J1)+NFPAR(3,J1)+NFPAR(4,J1)
   NNN      =NFPAR(2,J2)+NFPAR(3,J2)+NFPAR(4,J2)
   CALL BANDI(NNN,MMM)
   CALL GLIST(TAB(20),TAB(19),JMAX)
C   KRONECKER DELTA OVER NU(I),NU(J)
   IF(NLP(1).EQ.0) GO TO 65
   S=0.
   H1=0.
   EPOT=0.
   GO TO 53
C   KRONECKER DELTA OVER GERADE,UNGERADE
65 IF(MOD(NHUG,2).EQ.0) GO TO 1331
   KRONEK=MMM+NNN+NLP(3)
   IF(MOD(KRONEK,2).EQ.0) GO TO 1331
   S=0.
   H1=0.
   EPOT=0.
   GO TO 53
C   APPENDIX I = EQN (40)
1331 S=A(7)*B(5)-A(5)*B(7)
      C2=NLP(2)
      C3=NLP(3)
      C5=NLP(5)
      C6=NLP(6)
      C7=NLP(7)
ONE 260
ONE 270
ONE 280
ONE 290
ONE 300
ONE 310
ONE 320
ONE 330
ONE 340
ONE 350
ONE 360
ONE 370
ONE 380
ONE 390
ONE 400
ONE 410
ONE 420
ONE 430
ONE 440
ONE 450
ONE 460
ONE 470
ONE 480
ONE 490
ONE 500
ONE 510
ONE 520
ONE 530
ONE 540
ONE 550
ONE 560
ONE 570
ONE 580
ONE 590
ONE 600

```



```

C      APPENDIX I - EQN (41)
      EDEL T=A(6)*B(5)*(ZA+ZB)
C      APPENDIX I - EQN (42)
      EZETA= A(5)*B(6)*(ZA-ZB)
C      HERE TO STATEMENT 1332 - APPENDIX I - EQN. (43)
      EK1=B(5)*(FLP(2)*FLP(2)*A(7)-2.*(FLP(2)*C7+FLP(1))
      1*A(6)+2.*FLP(2)*C7*A(4)+(C5-C7*C7)*A(3))
      EK4=-4.0*C2*C2*(A(2)*B(1)-A(1)*B(2))
      EK2=-A(5)*(FLP(4)*FLP(4)*C(7,1)-2.*(FLP(4)*C6+FLP(3 ))*C(6,1)
      1+2.0*FLP(4)*C6*C(4,1)+(C3-C6*C6)*C(3,1))
      EK3=A(5)*C(5,1)*(C7*C7+C5-FLP(2)*FLP(2)-C6*C6-C3+FLP(4)*FLP(4))
      IF (MOD(NHUG,2).EQ.0) GO TO 1332
      FL1=1.
      IF (MOD(NNN,2).NE.0) FL1=-FL1
      EK2PRI=-A(5)*(FLP(3)*FLP(3)*C(7,2)-2.*(FLP(3)*C6+FLP(4))*C(6,2)
      1+2.*FLP(3)*C6*C(4,2)+(C3-C6*C6)*C(3,2))
      EK3PRI=A(5)*C(5,2)*(C7*C7+C5-FLP(2)*FLP(2)-C6*C6-C3+FLP(3)*FLP(3))
      EK2=EK2+FL1*EK2PRI
      EK3=EK3+FL1*EK3PRI
      EKIN=EK1+EK2+EK3+EK4
      EPOT=EDEL T+EZETA
1332 53 CONTINUE
      DO 55 I=1,18
      55 JTAB(I)=NLP(I)
      RETURN
      END
ONE 610
ONE 620
ONE 630
ONE 640
ONE 650
ONE 660
ONE 670
ONE 680
ONE 690
ONE 700
ONE 710
ONE 720
ONE 730
ONE 740
ONE 750
ONE 760
ONE 770
ONE 780
ONE 790
ONE 800
ONE 810
ONE 820
ONE 830
ONE 840
ONE 850
ONE 860

```



```

      FUNCTION TWOEL (TABA,TABB,G1,G2,NLP1,NLP2,R,NDIM,S)
      FUNCTION IS H2, OBTAINED BY MERGING THE 2 GINT LISTS, USING SIGMA AND
      C INDEX MAXIMA GIVEN IN NLP1 AND NLP2.
      C JMAX, NUMBER OF INTEGRATION POINTS, AND NMINUS, NUMBER TO BE
      C ACCUMULATED NEGATIVELY AT BEGINNING OF LIST, TO BE SUPPLIED
      C SEPARATELY AS CONSTANT INFORMATION.
      C APPENDIX I = EQN. (60), EXCEPT FOR KRONECKER DELTA OVER
      C SIGMA(1), = SIGMA(2), WHICH IS APPLIED IN FUNCTION TRX
      COMMON/DATBLS/D1(11,11),VD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
      1WT(40),NMINUS,RULE(2)
      DIMENSION TABA(1460),TABB(1460),NLP1(7),NLP2(7)
      DIMENSION G1(NDIM,36),G2(NDIM,36),S(16)
      11  L= MINU (NLP1(4))-IABS (NLP1(1)),NLP2(4)-IABS (NLP2(1))
      TWOEL= TABA(19)*TABB(19)
      L1 = NMINUS + 1
      DO 15 K=1,L
      IF(NMINUS.EQ.0) GO TO 16
      14 DO 13 K1=1,NMINUS
      13 TWOEL = TWOEL-G1(K1,K)*G2(K1,K)
      16 DO 15 K1 = L1,JMAX
      15 TWOEL = TWOEL+G1(K1,K)*G2(K1,K)
      TWOEL=2./R*TWOEL
      K=NLP1(8)
      L=NLP1(9)
      K1=NLP2(8)
      L1=NLP2(9)
      TWOEL=TWOEL/(S(K)*S(L)*S(K1)*S(L1))
      RETURN
      END

```

TWO 10
 TWO 20
 TWO 30
 TWO 40
 TWO 50
 TWO 60
 TWO 70
 TWO 80
 TWO 90
 TWO 100
 TWO 110
 TWO 120
 TWO 130
 TWO 140
 TWO 150
 TWO 160
 TWO 170
 TWO 180
 TWO 190
 TWO 200
 TWO 210
 TWO 220
 TWO 230
 TWO 240
 TWO 250
 TWO 260
 TWO 270
 TWO 280
 TWO 290


```

SUBROUTINE BANDI (MMM,NNN)
  GENERATES B AND BINT FOR PARAMETER ZETA
  A CONTAINS A INTEGRALS FOR ONE-ELECTRON CALCULATIONS

  INPUT  L1 = NLP(1)*SIGMA=NU(I)+NJ(J)
         L2=TAU
         L3=M(I)+M(J)
         L5=N(I)+N(J)

  OUTPUT B  B(1) = B(MS) FOR TAU(1), B(2) = B(MS+2) FOR TAU(1)
           B(3) TO B(7) = B(MS-2) TO B(MS+2) FOR NU1=NU2
           BINT(K,L) BLOCK - I INTEGRAL, L=1 FOR I(MS), L=2, I(MS+2)
           K GIVES LOWER INDEX, VALUE OF 1 STARTS AT K=MUS.
           L4=UPPER LIMIT OF MU SUMMATION IN NEUMANN EXPANSION
           D(I,J)=FACT(FLOAT(I-1))*FLOAT(2*J-1)/DFACT(FLOAT(I-J))/DFACT(FLOAT(BAI
           1(I+J-1))*((1.-FLOAT(I+J-((I+J)/2)*2))
           DD(I,J)=SQRT(FACT(FLOAT(I+J-2))*FLOAT(2*I-1)/FACT(FLOAT(I-J)))

  COMMON/SPACE/ IDUM(309)
  COMMON/WORK/L1,L2,L3,L4,L5,L6,L7,NOTA(5),DELT(2),ZETA(2),UL(2),
    *A(7),F(7),BINI(36,2),B(7,2),
    95(38,11,2),R(60),
    8 C,C1,J,K,L,M,K1,K2,K3,K4,K5,NIXIT,NUTS,IX,IY,IZ,NO,MMA,PAX,
    71,TEMP(426),ZG1(1470), RMDR(9588)
  COMMON/DABLS/D (11,11),DD (36,7),DD2(43,7),JMAX,WTINF,POINT(40),
    1WT(40),NMINUS,RULE(2)
  DIMENSION X(60)
  EQUIVALENCE(IDUM(5), NHUG) , (X,R),(LL,IX) ,(DELTA,DELT(1))
  EQUIVALENCE(IDUM(22),IOUT)
  NIXIT = IABS(L1)
  NO=1
  DO 102 I=1,936
    102 A(I)=0.
    IF((L3.GT.8).OR.(L2.GT.3).OR.(NIXIT.GT.6)) GO TO 6
    1 IF( ABS(ZETA(NO)).GE.1.E-5) GO TO 1290

```



```

C   MAKE I(O,ZETA,O) FOR VERY SMALL ZETA
      K1 = 2+NIXIT
      S(1,1,NO) = 2.
      DO 127 K=2,K1
        C=2*K-1
      127 S(K,1,NO) = -S(K-1,1,NO) / C
        S(K1,1,NO) = S(K1,1,NO)*ZETA(NO)
        K1 = K1+1
      DO 1280 K=K1,38
      1280 S(K,1,NO) = 0.
        GO TO 1311
      1290 M=28.+ABS(ZETA(NO)/1.95)
        IF(M,GT,60) GO TO 6
      C   MAKE I FOR M AND TAU ZERO
      1291 R(1) = 0.
        DO 1300 K=2,M
          C=2*(M-K)+3
      1300 R(K) = -ZETA(NO)/(C-ZETA(NO)*R(K-1))
          S(1,1,NO)=2.*EXP(ABS(ZETA(NO)))*ZETA(NO)**(-NIXIT)/(1.+ABS(ZETA(NO)
          1)))-ZETA(NO)*R(M)
          DO 1310 K=1,37
            L=M-K+1
      1310 S(K+1,1,NO) = S(K,1,NO)*R(L)
      1311 IF(MOD(NHUG,2).EQ,0) GO TO 100
      C   MAKE I(M,ALFPR1,TAU) , APPENDIX I - EQN.(55)
        NO = NO+1
        IF(NO,EQ,2) GO TO 1
      C   MAKE COEFFICIENTS FOR M AND TAU CALCULATION
        100 DO 1315 K=1,36
          C=K-NIXIT
          C1=2*K+1
      1315 R(K)=C/C1
      C   ADVANCE TAU AND IF SIGMA ZERO, PREPARE B
        K4=37
        IF(L2,EQ,0) GO TO 1400

```

```

BAI 360
BAI 370
BAI 380
BAI 390
BAI 400
BAI 410
BAI 420
BAI 430
BAI 440
BAI 450
BAI 460
BAI 470
BAI 480
BAI 490
BAI 500
BAI 510
BAI 520
BAI 530
BAI 540
BAI 550
BAI 560
BAI 570
BAI 580
BAI 590
BAI 600
BAI 610
BAI 620
BAI 630
BAI 640
BAI 650
BAI 660
BAI 670
BAI 680
BAI 690
BAI 700

```



```

1320 K1=L2-1
1325 IF(K1) 1400,1330,1340
1330 IF(L1.NE.0) GO TO 1340
C CALCULATE B FOR NU=1
1332 K2=L3+1
      K3=L3-2*(L3/2)+1
      B(1,1)=0.
      B(1,2)=0.
      DO 1333 K=K3,K2,2
      DO 1333 NU=1,2
1333 B(1,NO)=B(1,NO)+D(K2,K)*S(K,1,NO)
      K2=K2+2
      B(2,1)=0.
      B(2,2)=0.
      DO 1334 K=K3,K2,2
      DO 1334 NO = 1,2
1334 B(2,NO)=B(2,NO)+D(K2,K)*S(K,1,NO)
1340 K1=K1-1
C ADVANCE TAU BY 1
1350 DO 1360 J=1,2
      DO 1360 NO=1,2
      S(1,J+1,NO)=S(2,J,NO)
      K4=K4-1
      DO 1360 K=1,K4
1360 S(K+1,J+1,NO)=S(1,-R(K))*S(K+2,J,NO)+R(K)*S(K,J,NO)
      K5=K4+1
      DO 1370 K=1,K5
      DO 1370 NO=1,2
1370 S(K,1,NO)=S(K,1,NO)-S(K,3,NO)
      GO TO 1325
1400 IF(L1.NE.0) GO TO 1440
C CALCULATE B FOR NU EQUALS NU
      K1=1
      IF(L3.GT.1) K1=L3-1
1410 K2=L3+3

```

```

BAI 710
BAI 720
BAI 730
BAI 740
BAI 750
BAI 760
BAI 770
BAI 780
BAI 790
BAI 800
BAI 810
BAI 820
BAI 830
BAI 840
BAI 850
BAI 860
BAI 870
BAI 880
BAI 890
BAI 900
BAI 910
BAI 920
BAI 930
BAI 940
BAI 950
BAI 960
BAI 970
BAI 980
BAI 990
BAI 1000
BAI 1010
BAI 1020
BAI 1030
BAI 1040
BAI 1050

```



```

DO 1420 J=K1,K2
DO 1420 NO = 1,2
K5=J-K2+7
K3=J-2*((J-1)/2)
B(K5,NO)=0.
DO 1420 K=K3,J,2
1420 B(K5,NO)=B(K5,NO)+D(J,K)*S(K,1,NO)
C ADVANCE M TO FINAL VALUES
1440 K2=K3+2
DO 1450 J=1,K2
DO 1450 NO = 1,2
S(1,J+1,NO)=S(2,J,NO)
K4=K4-1
DO 1450 K=1,K4
1450 S(K+1,J+1,NO)=(1.-R(K))*S(K+2,J,NO)+R(K)*S(K,J,NO)
IF(MOD(NHUG,2).EQ.0) GO TO 1600
PAX=1.
IF((MMM-(MMM/2)*2).NE.0) PAX=-PAX
DO 1501 IX=1,38
DO 1501 IY=1,11
1501 S(IX,IY,1)=(S(IX,IY,1)+PAX*S(IX,IY,2))
DO 1502 IX=1,7
1502 F(IX)=B(IX,1)+PAX*B(IX,2)
C MULTIPLY BY DD COEFFICIENTS
1500 K5=K4+1
K1=NIXIT + 1
DO 1455 J=K1,K5
S(J,K2-1,1) = DD(J,K1)*S(J,K2-1,1)
1455 S(J,K2+1,1) = DD(J,K1)*S(J,K2+1,1)
C TEST FOR CUT-OFF INDEX VALUE OR NON-CONVERGENCE
C=0.
DO 1460 K=K1,K5
1460 C=AMAX1(C,ABS(S(K,K2-1,1)),ABS(S(K,K2+1,1)))
C=1.E-5*C
DO 1463 K=1,K5
BAI 1060
BAI 1070
BAI 1080
BAI 1090
BAI 1100
BAI 1110
BAI 1120
BAI 1130
BAI 1140
BAI 1150
BAI 1160
BAI 1170
BAI 1180
BAI 1190
BAI 1200
BAI 1210
BAI 1220
BAI 1230
BAI 1240
BAI 1250
BAI 1260
BAI 1270
BAI 1280
BAI 1290
BAI 1300
BAI 1310
BAI 1320
BAI 1330
BAI 1340
BAI 1350
BAI 1360
BAI 1370
BAI 1380
BAI 1390
BAI 1400

```



```

1463 CONTINUE
1470 IF(L4.EQ.K5) GO TO 1498
C FINAL STORAGE OF INTEGRALS
1471 IF(MOD(NHJG,2).EQ.0) GO TO 1504
C KRONECKER DELTA OF EQN. (55)
MMA=MMM+NNN+L3 - NIXIT
DO 1505 IX= K1,K5
NUTS = MMA + IX -1
NUTS=NUTS-(NUTS/2)*2
IF(NUTS.EQ.0) GO TO 1505
S(IX,K2+1,1) = 0.
S(IX,K2-1,1) = 0.
1505 CONTINUE
1504 DO 1480 K=K1,L4
J=K+1-K1
BINT(J,1)=S(K,K2-1,1)
BINT(J,2)=S(K,K2+1,1)
1480 NTA(5)=19+JMAX*(L4-NIXIT)
C MAKE A SUB N INTEGRALS - EQNS.(38,38PRIME,44)
LL=L5+2*L2+2
IF(NIXIT.NE.0) RETURN
X(1)=EXP (-DELTA)/DELTA
DO 1860 K=1,LL
C=K
1860 X(K+1)=X(1)+C*X(K)/DELTA
K5=L5+1
IF(L2.EQ.0) GO TO 1890
1862 K3=L2-1
K2=LL+1
1863 IF(K3)1890,1864,1870
1864 A(1)=X(K5)
A(2)=X(K5+2)
BAI 1410
BAI 1420
BAI 1430
BAI 1440
BAI 1450
BAI 1460
BAI 1470
BAI 1480
BAI 1490
BAI 1500
BAI 1510
BAI 1520
BAI 1530
BAI 1540
BAI 1550
BAI 1560
BAI 1570
BAI 1580
BAI 1590
BAI 1600
BAI 1610
BAI 1620
BAI 1630
BAI 1640
BAI 1650
BAI 1660
BAI 1670
BAI 1680
BAI 1690
BAI 1700
BAI 1710
BAI 1720
BAI 1730
BAI 1740
BAI 1750

```



```

1870 K3=K3-1
      K2=K2-2
      DO 1880 K=1,K2
1880  X(K)=X(K+2)-X(K)
      GO TO 1863
1890  IF(L5-1) 1893,1892,1891
1891  A(3)=X(K5-2)
1892  A(4)=X(K5-1)
1893  A(5)=X(K5)
      A(6)=X(K5+1)
      A(7)=X(K5+2)
      RETURN
1498  WRITE(IOUT,7)
      CALL EXIT
      6  WRITE(IOUT,9) L2,L3,NIXIT,M
      CALL EXIT
      7  FORMAT(1H020X,17HBANDI-NO CONVERGE )
      9  FORMAT(1H020X,16HBANDI-PARAMS OUT 415)
      C  B LOOP FOR HETERONUCLEAR CASE
1600  DO 1604 I=1,7
1604  F(I) = B(I,1)
      GO TO 1500
      END

```

```

BAI 1760
BAI 1770
BAI 1780
BAI 1790
BAI 1800
BAI 1810
BAI 1820
BAI 1830
BAI 1840
BAI 1850
BAI 1860
BAI 1870
BAI 1880
BAI 1890
BAI 1900
BAI 1910
BAI 1920
BAI 1930
BAI 1940
BAI 1950
BAI 1960
BAI 1970
BAI 1980

```



```

10  SUBROUTINE GLIST(GINT,GT,NDIM)
20  INPUT-- SCREENING PARAMETER DELTA,MUST BE GREATER THAN +1.E-2.
30  BINT, LIST OF I INTEGRALS OUTPUT FROM BANDI PROGRAM
40  L1=SIGMA (MAY BE EITHER SIGN), L2=TAU, L5=N,
50  L4=MAXIMUM INDEX VALUE USED (STARTING FROM SIGMA=0). L4 IS
60  PRODUCED AS OUTPUT IN BANDI PROGRAM.
70  OUTPUT-- GINT CONTAINS OUTPUT VALUES FOR TWO-ELECTRON INTEGRALS, IN
80  A NUMBER DETERMINED BY L4 AND WPTBL(FROM GLIST PRO.).GLI
90  USES CONSTANT DATA BLOCK DATBLS, ASSEMBLED SEPARATELY
100 /DATBLS/ CONTAINS NO. POINTS,BLOCK FOR 40 POINTS
110 BLOCK FOR CORRESPONDING 40 WEIGHTS, NO. OF INITIAL POINTS ENTERING
120 WITH MINUS SIGN IN SCALAR PRODUCT FORMATION.
130
140  ARRAY S(I,J)=K(MU,SIGMA) OF EQN. (56)
150  ARRAY GINT IS THE ARRAY OF G(I,K) INTEGRALS DEFINED BY
160  EQNS. (57-59)
170
180  D(I,J)=FLOAT(2*I-1)/FLOAT(I+J-1)
190  DD(I,J)=FLOAT(I+J-1)*FLOAT(I-J+1)/FLOAT(4*I*I-1)
200  COMMON/SPACE/ IDUM(309)
210  COMMON/WORK/L1,L2,L3,L4,L5,L6,L7,NOTA(5),DELTA,ZETA(5),A(7),B(7),
220  *BINT(36,2),CX(7,2),
230  2X(44), FRAT(45,14),S(45,11),
240  3 C,CC,R,TEE,L,J,LL,LM,LN,K,K1,K2,K3,K4,K5,K6,KK9,CL,CK,IP,
250  4REST(153),ZG1(1470),RMDR(9588)
260  COMMON/DATBLS/D1(11,11),DD(36,7),DD(43,7),JMAX,WTINF,POINT(40),
270  1WT(40),NMINUS,RULE(2)
280  DIMENSION GINT(NDIM,36)
290  EQUIVALENCE (IOUT,IDUM(22))
300  DO 1984 J=1,1189
310  1984 X(J)=0.
320  LL=L5+2*L2+2
330  LM=L4+LL
340  LN=LM-1
350  K1=IABS(L1)

```



```

360 GLI
370 GLI
380 GLI
390 GLI
400 GLI
410 GLI
420 GLI
430 GLI
440 GLI
450 GLI
460 GLI
470 GLI
480 GLI
490 GLI
500 GLI
510 GLI
520 GLI
530 GLI
540 GLI
550 GLI
560 GLI
570 GLI
580 GLI
590 GLI
600 GLI
610 GLI
620 GLI
630 GLI
640 GLI
650 GLI
660 GLI
670 GLI
680 GLI
690 GLI
700 GLI

IF((L5.GT.8).OR.(LM.GE.45).OR.(DELTA.LT.0.01)) GO TO 11
DO 1842 J=1,JMAX
  R=0.0
  TEE=DELTA*POINT(J)
  IF(TEE.LT.128.)R=WT(J)*EXP(-TEE)/DELTA
  TEE=TEE-DELTA
  1700 X(1)=POINT(J)
  1701 DO 1702 K=2,LM
  1702 X(K)=POINT(J)-DD(K-1,1)/X(K-1)
  C LARGE Y*DELTA. KO AND K1
    S(1,1)=WT(J)*EXP (-DELTA)/DELTA - R
    S(2,1)=S(1,1)*(DELTA+1.)/DELTA+R*(1.-POINT(J))/POINT(J)
  C LARGE Y*DELTA. REMAINING K
    DO 1710 K=2,LN
    C=K
    1710 S(K+1,1)=((S(K-1,1)+R)*C*(POINT(J)-X(K))/(C-1.)+C*S(K,1))/DELTA /
      1 X(K)-R
    IF(K1.EQ.0) GO TO 1810
  C NON-ZERO SIGMA. LARGE Y*DELTA. MAKE F
    1720 K2=K1+1
    DO 1721 L=K2,LM
    FRAT(L,1)=1.0
    C=L
    1721 FRAT(L,2)=(X(L)*(2.0*C-1.0)/C-POINT(J))*DELTA/(C-1.0)
    KK9=K2-2
    IF(KK9) 1741,1741,1730
  1730 C=(POINT(J)**2-1.0)*DELTA
    DO 1740 L=K2,LM
    CL=L
    DO 1740 K=1,KK9
    CK=K
    1740 FRAT(L,K+2)=(-2.0*CK*POINT(J)*FRAT(L,K+1)+C*FRAT(L,K))*DELTA/((CL-GLI
      1 CK-1.0)*(CL+CK))
    1741 CONTINUE
  C LARGE Y*DELTA. MAKE K SUB SIGMA

```



```

DO 1760 K=K2,LN
CC=FRAT(K,2)
IF(K2=2) 1999,1750,1742
1742 DO 1744 L=3,K2
1744 CC=CC+FRAT(K,L)
1750 C=C1
IP = K1
1760 S(K,1)=((SQRT(POINT(J)*POINT(J)-1.))**IP)*(S(K,1)*FRAT(K,1)-R*CC)/
XFRAT(K,K2)
C SEE IF NEW X COEFFICIENTS ARE NEEDED
IF(K1.EQ.0) GO TO 1810
C NEW X COEFFICIENTS ARE NEEDED
1800 C=C1
X(1)=C+POINT(J)
K2=K1+1
DO 1803 K=2,LN
1803 X(K)=POINT(J)-DD(K-1,K2)/X(K-1)
C ADVANCE M AND TAU
1810 K5=L2
K2=K1+2
K3=LM
K4=K1+1
IF(L2.EQ.0) GO TO 1830
1811 K6=3
1812 DO 1820 L=2,K6
S(K1+1,L)=POINT(J)*S(K2,L-1)
K3=K3+1
DO 1820 K=K2,K3
1820 S(K,L)=X(K)*S(K+1,L-1)+(POINT(J)-X(K))*S(K-1,L-1)
K5=K5+1
IF(K5) 1840,1822,1822
1822 DO 1824 K=K4,K3
1824 S(K,1)=S(K,3)-S(K,1)
IF(K5) 1999,1830,1812
1830 K6=L5+3

```

GLI 710
GLI 720
GLI 730
GLI 740
GLI 750
GLI 760
GLI 770
GLI 780
GLI 790
GLI 800
GLI 810
GLI 820
GLI 830
GLI 840
GLI 850
GLI 860
GLI 870
GLI 880
GLI 890
GLI 900
GLI 910
GLI 920
GLI 930
GLI 940
GLI 950
GLI 960
GLI 970
GLI 980
GLI 990
GLI 1000
GLI 1010
GLI 1020
GLI 1030
GLI 1040
GLI 1050


```

      GO TO 1812
C   COMBINE THESE RESULTS WITH I INTEGRALS
1840 IF(K3.NE.L4) GO TO 1999
1841 DO 1842 K=K4,K3
      L=K-K4+1
1842 GINT(J,L)=S(K,K6)*BINT(L,1)-S(K,K6-2)*BINT(L,2)
C   POINT AT INFINITY
1844 GT = 0.
      IF(K1.EQ.0)GT=WTINF*(A(7)*BINT(1,1)-A(5)*BINT(1,2))
      RETURN
1999 WRITE(IOUT,18)
      CALL EXIT
11  WRITE(IOUT,19) DELTA,L5,LM
      CALL EXIT
18  FORMAT(1H020X,17HGLIST-GENERAL ERR )
19  FORMAT(1H020X,16HGLIST-PARAMS OUTF10.4,214)
      END
GLI 1060
GLI 1070
GLI 1080
GLI 1090
GLI 1100
GLI 1110
GLI 1120
GLI 1130
GLI 1140
GLI 1150
GLI 1160
GLI 1170
GLI 1180
GLI 1190
GLI 1200
GLI 1210
GLI 1220

```

```

**      ***      ***      ***      ***      ***      ***      ***      ***      ***
C   SUBROUTINE MATRIX (INPT,LCON,NUMBR,NEL)
C   CONTROLLING PROGRAM OF MATRIX   BRANCH
C   COMBINES UTAPE AND S1, H1, H2 TO MAKE TOTAL S, H
C   ZS1=S(P)   EQN (31)
C   ZH= H(P)   EQN (32)
C   S1      EQN (35)
C   H1      EQN (34,37)
C   H2      EQN (36,60)
C   COMMON/SPACE/LA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,MTX
2LSRCH,JKW3,LIAR,STEP1,STEP2,EQ,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)MTX
3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG( 6),ICTAG(64),
4DELT(25),HMAX,RMIN,RSTEP,STEP3
COMMON/WORK/H2(9317),UMAT(28,28),IPER(20),IDEN(3), I,J,K ,
1L,L1,L2,L3,L4,K1,K2,K3,K4,K5,IP,I1,JJ, IZ,ZS1,ZH ,IE1,IE2,ICON1,
2 ICON2,KIK,KJL,DOM(19),S(903),H(903),SPRI(136),HPRI(136),S1(136),
IH1(136)
COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)
**      ***      ***      ***      ***      ***      ***      ***      ***      ***
MTX 10
MTX 20
MTX 30
MTX 40
MTX 50
MTX 60
MTX 70
MTX 80
MTX 90
MTX 100
MTX 110
MTX 120
MTX 130
MTX 140
MTX 150
MTX 160
MTX 170
MTX 180

```



```

EQUIVALENCE (OLP,H2),(HAM,H2(1765))
EQUIVALENCE(IO,LSPARE)
DIMENSION OLP(42,42),HAM(42,42),LCON(NUMBR,NEL)
C
IND2(I,K)=MINO(I,K)+(MAXO(I,K)*(MAXO(I,K)-1)/2)
C
1 FORMAT(8E15.7)
NMAT=NCON*ND
CALL TXFORM(SPRI,UMAT,IPER,DOM,NFPAR,ITX,NFCN,INPT,HPRI)
CALL TRANS (S1,H1,SPRI,HPRI)
IF(ITX.EQ.2) GO TO 1314
L4=(MMAT*(MMAT+1))/2
WRITE(IO,1) (S1(I),I=1,MMAT)
WRITE(IO,1) (H1(I),I=1,MMAT)
WRITE(IO,1) (H2(I),I=1,L4)
IF(NOTRF.EQ.0) GO TO 1314
WRITE(IO,1) (SPRI(I),I=1,MMAT)
WRITE(IO,1) (HPRI(I),I=1,MMAT)
1314 CONTINUE
IZ=0
LI=0
DO 401 L=1,NMAT
DO 401 K=1,L
LI=LI+1
H(LI)=0.
S(LI)=0.
401 CONTINUE
READ(NT) IDEN
IF(IDEN(3).NE. JCODE) GO TO 1999
DO 411 IP=1,NPERMS
READ (NT) (IPER(I),I=1,N),((UMAT(K,J),K=1,ND),J=1,ND)
DO 412 ICON1=1,NCON
II = (ICON1-1)*ND
MU=ICON1
IF((IABS(NHUG).EQ.2).AND.(ICON1.GT.(NCON/2))) MU=NCON/2

```

MTX 190
MTX 200
MTX 210
MTX 220
MTX 230
MTX 240
MTX 250
MTX 260
MTX 270
MTX 280
MTX 290
MTX 300
MTX 310
MTX 320
MTX 330
MTX 340
MTX 350
MTX 360
MTX 370
MTX 380
MTX 390
MTX 400
MTX 410
MTX 420
MTX 430
MTX 440
MTX 450
MTX 460
MTX 470
MTX 480
MTX 490
MTX 500
MTX 510
MTX 520
MTX 530

Line	Code	Statement	Label
54	MTX	DO 412 ICON2=1,MU	
55	MTX	JJ=(ICON2-1)*ND	
56	MTX	406 IZ = 0	
57	MTX	ZS1 = 1.	
58	MTX	DO 413 IE1 = 1,N	
59	MTX	I = LCON(ICON1,IE1)	
60	MTX	L1 = IPER(IE1)	
61	MTX	K = LCON(ICON2,L1)	
62	MTX	L2=IND2(I,K)	
63	MTX	IF(S1(L2).EQ.0.) GO TO 414	
64	MTX	ZS1 = ZS1+S1(L2)	
65	MTX	GO TO 413	
66	MTX	414 IZ = IZ+1	
67	MTX	IF (IZ-2) 415,416,412	
68	MTX	415 K1=1	
69	MTX	K2=K	
70	MTX	K5=IE1	
71	MTX	KIK=L2	
72	MTX	GO TO 413	
73	MTX	416 K3=1	
74	MTX	K4=K	
75	MTX	KJL=L2	
76	MTX	413 CONTINUE	
77	MTX	IF(IZ-1) 420,421,422	
78	MTX	NO OVERLAP WAS ZERO	
79	MTX	420 ZH = 0.	
80	MTX	DO 423 IE1=1,N	
81	MTX	I = LCON(ICON1,IE1)	
82	MTX	L1 = IPER(IE1)	
83	MTX	K=LCON(ICON2,L1)	
84	MTX	L2 = IND2(I,K)	
85	MTX	ZH=ZH+H1(L2) / S1(L2)	
86	MTX	DO 419 IE2=1,IE1	
87	MTX	IF(IE1.EQ.IE2) GO TO 423	
88	MTX	J=LCON(ICON1,IE2)	


```

      L3 = IPER(IE2)
      L = LCON(ICON2,L3)
      ZH=ZH+TRX(I,J,K,L,H2,S1)
419 CONTINUE
423 GO TO 426
      ONE OVERLAP INTEGRAL = 0. ELECTRON NO. STORED IN L3
421 ZH=H1(KIK)
      DO 425 IE2=1,N
      IF(IE2.EQ.K5) GO TO 425
      J=LCON(ICON1,IE2)
      L1=IPER(IE2)
      L=LCON(ICON2,L1)
      ZH=ZH+TRX(K1,J,K2,L,H2,S1)
425 CONTINUE
      GO TO 426
      TWO FACTORS WITH ZERO OVERLAP
422 ZH=TRX(K1,K3,K2,K4,H2,S1)
      IF(ZH.EQ.0.) GO TO 412
426 ZH=ZH*ZS1
      STORE ZS1,ZH*UMAT(I,J) IN D*D BLOCKS, INDEXED AS A ROW VECTOR
      DO 424 I=1,ND
      L1 = I+I
      L1=(L1*(L1-1))/2
      KJL=ND
      IF(I1.EQ.JJ) KJL=I
      DO 424 J=1,KJL
      L2=JJ+J+L1
      IF (J2.GT.0) GO TO 424
      S( L2)= S( L2) + UMAT(I,J)*ZS1
424 H( L2)= H( L2) + UMAT(I,J)*ZH
412 CONTINUE
411 CONTINUE
      L1=0
      DO 500 I=1,NMAT
      DO 500 J=1,I

```

```

MTX 890
MTX 900
MTX 910
MTX 920
MTX 930
MTX 940
MTX 950
MTX 960
MTX 970
MTX 980
MTX 990
MTX 1000
MTX 1010
MTX 1020
MTX 1030
MTX 1040
MTX 1050
MTX 1060
MTX 1070
MTX 1080
MTX 1090
MTX 1100
MTX 1110
MTX 1120
MTX 1130
MTX 1140
MTX 1150
MTX 1160
MTX 1170
MTX 1180
MTX 1190
MTX 1200
MTX 1210
MTX 1220
MTX 1230

```



```

L1=L1+1
HAM(I,J)=H(L1)
OLP(I,J)=S(L1)
OLP(J,I)=S(L1)
500 HAM(J,I)=H(L1)
C INVERT TOTAL MOLECULAR FUNCTION AND PICK G OR U - EQN (16)
IF(IABS(NHUG).NE.2) RETURN
KIK=NCNCON/2
KJL=NMAT/2
DO 512 ICON1=1,KIK
II=(ICON1-1)*ND
JJ=II+KJL
IZ=0
DO 513 I=1,N
JELCON(ICON1,I)
513 IZ=IZ+NFPAR(2,J)+NFPAR(3,J)
IP=ISIGN(1,NHUG)
IF(MOD(IZ,2).NE.0) IP=-IP
ZH=IP
DO 514 I=1,ND
L1=II+I
L2=JJ+I
DO 514 J=1,KJL
OLP(L1,J)=OLP(L1,J)+ZH*OLP(L2,J)
514 HAM(L1,J)=HAM(L1,J)+ZH*HAM(L2,J)
512 CONTINUE
NMAT=NMAT/2
C HAM,OLP ARE CARRIED OVER INTACT TO SEARCH
RETURN
C FORTRAN TAPE KUCKING MACRO TO CORRECT TAPE POSITION ERRORS
C CONSISTENTLY MADE BY HONEYWELL AUTOMATH 1800 MONITOR
1999 IF(IZ.EQ.1313) CALL EXIT
WRITE(10,105) JCODE,IDEN(3)
IZ=1313
REWIND NT
MTX 1240
MTX 1250
MTX 1260
MTX 1270
MTX 1280
MTX 1290
MTX 1300
MTX 1310
MTX 1320
MTX 1330
MTX 1340
MTX 1350
MTX 1360
MTX 1370
MTX 1380
MTX 1390
MTX 1400
MTX 1410
MTX 1420
MTX 1430
MTX 1440
MTX 1450
MTX 1460
MTX 1470
MTX 1480
MTX 1490
MTX 1500
MTX 1510
MTX 1520
MTX 1530
MTX 1540
MTX 1550
MTX 1560
MTX 1570
MTX 1580

```



```

GO TO 410
105 FORMAT(1H020X,15HWRONG PERM TAPE216)
END
**      ***      ***      ***      ***      ***      ***      ***
C      SUBROUTINE TXFORM(S1,S,NORD,IORD,NFPAR,ITX,N,IN,H1)
C      PREPARE TRANSFORMATION MATRIX
C      THE TAG NOTRF DETERMINES THE TYPE TRANS.
C      NOTRF.LT.0 - CONSTANT TRANS BY INPUT CARDS
C      NOTRF.EQ.0 - NO TRANSFORMATION
C      NOTRF.GT.0 - TRANSFORMATION IS TO BE CALCULATED
C      COMMON/CIJ/C(16,16),NOTRF,NU,MU,I,J,K,L,HH,JUNK(4)
C      DIMENSION S1(136),S(16,16),NORD(16),IORD(16),NFPAR(6,16)
C      DIMENSION H1(136)
C      IND2(I,K)=MINO(I,K)+((MAXO(I,K)-1)/2)
C      IF(NOTRF.LE.0) RETURN
50 IF(NOTRF.EQ.1) GO TO 54
L=0
DO 55 I=1,N
DO 55 J=1,I
L=L+1
55 S(J,I)=S1(L)
GO TO 63
54 L=0
DO 51 I=1,N
DO 51 J=1,I
L=L+1
S(I,J)=0.
S(J,I)=0.
IF(I.EQ.J) S(I,I)=S1(L)
51 CONTINUE
K=NU+1
DO 52 I=K,N
DO 52 J=1,NU
IF(NFPAR(5,I).EQ.0) GO TO 52
L=IND2(I,J)
S(J,I)=S1(L)

```

```

MTX 1590
MTX 1600
MTX 1610
***
TXF 10
TXF 20
TXF 30
TXF 40
TXF 50
TXF 60
TXF 70
TXF 80
TXF 90
TXF 100
TXF 110
TXF 120
TXF 130
TXF 140
TXF 150
TXF 160
TXF 170
TXF 180
TXF 190
TXF 200
TXF 210
TXF 220
TXF 230
TXF 240
TXF 250
TXF 260
TXF 270
TXF 280
TXF 290
TXF 300
TXF 310
TXF 320

```



```

52 CONTINUE
63 NORD(1)=1313
   CALL D23CHO(N,S,C,C,C,IORD,NORD,16)
   DO 64 I=1,N
   DO 64 J=1,N
64 C(I,J)=S(J,I)
   RETURN
   END

**      ***      ***      ***      ***      ***      ***
SUBROUTINE TRANS (SPRI,HPRI,S1,H1)
C   APPLIES A TRANSFORMATION C(I,J) IN /CIJ/ TO H1,S1. STORING
C   THE RESULT IN THE LAST 272 WORDS OF /WORK/
C   TRANSFORMATION IS SUPPLIED ELSEWHERE BY INPUT CONSTANTS OR CALC.
COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
INPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,TRA
2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2),TRA
3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),
4DELT(25),RMAX,RMIN,RSTEP,STEP3
COMMON/CIJ/C(16,16),NOTRF,NU,MU,I,J,K,L,LI,HH,SS,CO,SAM
DIMENSION SI(136),H1(136),SPRI(136),HPRI(136)
IND2(I,K)=MINO(I,K)+(MAXO(I,K)*(MAXO(I,K)-1)/2)
IF(NOTRF.NE.O) GO TO 10
DO 11 I=1,MMAT
  HPRI(I)=H1(I)
11 SPRI(I)=SI(I)
  RETURN
10 L1=0
  SAM=1.E+10
  DO 1 I=1,NFCN
  DO 1 K=1,I
    L1=L1+1
  HH=0.
  SS=0.
  DO 2 J=1,NFCN
  IF(C(I,J).EQ.O.) GO TO 2
  DO 3 L=1,NFCN

```

TXF 330
TXF 340
TXF 350
TXF 360
TXF 370
TXF 380
TXF 390
TXF 400

*** TRA 10
*** TRA 20
*** TRA 30
*** TRA 40
*** TRA 50
*** TRA 60
*** TRA 70
*** TRA 80
*** TRA 90
*** TRA 100
*** TRA 110
*** TRA 120
*** TRA 130
*** TRA 140
*** TRA 150
*** TRA 160
*** TRA 170
*** TRA 180
*** TRA 190
*** TRA 200
*** TRA 210
*** TRA 220
*** TRA 230
*** TRA 240
*** TRA 250
*** TRA 260
*** TRA 270


```

280 TRA
290 TRA
300 TRA
310 TRA
320 TRA
330 TRA
340 TRA
350 TRA
360 TRA
370 TRA
380 TRA
390 TRA
400 TRA
410 TRA
420 TRA
430 TRA
440 TRA

```

```

IF(C(K,L).EQ.0.) GO TO 3
INDX=IND2(J,L)
CO = C(I,J)*C(K,L)
SS=SS+CO*S1(INDX)
HH=HH+CO*H1(INDX)
3 CONTINUE
2 CONTINUE
IF((K.EQ.I).AND.(SS.LT.SAM)) SAM=SS
SPRI(L1)=SS
HPRI(L1)=HH
1 CONTINUE
SAM=1.E-7*SAM
DO 4 I=1,MMAT
IF(SPRI(I).LE.SAM) SPRI(I)=0.
4 CONTINUE
RETURN
END

```

```

**      ***      ***      ***      ***      ***      ***      ***
FUNCTION TRX(I,J,K,L,H2,S1)
C      CALCULATES THE TRANSFORMED TWO-ELECTRON INTEGRALS UNDER THE
C      TRANSFORM C(I,J) STORED IN /CIJ/
C      THE TRANSFORM IS DEFINED AS FOLLOWS  X(K)=(SUM(L) OF(C(K,L)*XPRI(L)
COMMON/SPACE/LA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,TRX
2LSRCH,JKW3,LJAR,STEP1,STEP2,E0,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)TRX
3 ,FPA0(2,16),FPA0(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8), TRX
4DELT(25),RMAX,RMIN,RSTEP,STEP3
COMMON/CIJ/C(16,16),NOTRF,NU,MU,I1,J1,K1,L1,IDX1,IDX2,IDX3,M1,M2
DIMENSION H2(9317),S1(136)
IND2(I,K)=MIN0(I,K)+(MAX0(I,K)*(MAX0(I,K)-1)/2)
TRX=0.
M1=IND2(I,K)
M2=IND2(J,L)
IF(NOTRF.NE.0) GO TO 10
IF((NFPAR(3,I)-NFPAR(3,K)+NFPAR(3,J)-NFPAR(3,L)).NE.0) RETURN
IDX1=IND2(M1,M2)

```

```

**      10
**      20
**      30
**      40
**      50
**      60
**      70
**      80
**      90
**     100
**     110
**     120
**     130
**     140
**     150
**     160
**     170
**     180

```



```

    TRX=H2(IDX1)
    GO TO 11
10 DO 1 I=1,NFCN
    IF(C(I,I1).EQ.0.) GO TO 1
    DO 2 J=1,NFCN
    IF(C(J,J1).EQ.0.) GO TO 2
    DO 3 K=1,NFCN
    IF(C(K,K1).EQ.0.) GO TO 3
    DO 4 L=1,NFCN
    IF(C(L,L1).EQ.0.) GO TO 4
    IF((NFPAR(3,I1)-NFPAR(3,K1)+NFPAR(3,J1)-NFPAR(3,L1)).NE.0) GO TO 5
    IDX1=IND2(I1,K1)
    IDX2= IND2(J1,L1)
    IDX3= IND2(IDX1,IDX2)
    TRX=TRX+C(I,I1)*C(J,J1)*C(K,K1)*C(L,L1)*H2(IDX3)
5 CONTINUE
4 CONTINUE
3 CONTINUE
2 CONTINUE
1 CONTINUE
11 IF(NOTR.F.GT.0) RETURN
    IF(S1(M1).NE.0.) TRX=TRX/S1(M1)
    IF(S1(M2).NE.0.) TRX=TRX/S1(M2)
    RETURN
    END

```

```

TRX 190
TRX 200
TRX 210
TRX 220
TRX 230
TRX 240
TRX 250
TRX 260
TRX 270
TRX 280
TRX 290
TRX 300
TRX 310
TRX 320
TRX 330
TRX 340
TRX 350
TRX 360
TRX 370
TRX 380
TRX 390
TRX 400
TRX 410
TRX 420
TRX 430

```



```

SUBROUTINE SEARCH
CONTROLLING PROGRAM OF SEARCH      BRANCH
ENERGY CALCULATION AND PARAMETER SEARCH LINK

COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,SCH
2LSRCH,JKW3,L1AR,STEP1,STEP2,E0,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)SCH
3 ,FPAR0(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),SCH
4FELT(25),RMAX,RMIN,KSTEP,STEP3SCH
COMMON/WORK/OVRLAP(42,42),HAMILT(42,42),COET(42,42),COETO(42,42),SCH
*OVP(42,42),HAM(42,42),E(42),E1(42),E2(42),E3(42),KO,I,J,TEMP,NE1,SCH
XFINK(1760),SIGSCH
COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),SCH
1WT(40),NMINUS,RULE(2)SCH
COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)SCH
DIMENSION D(6),Z(6),ENERG(6),X(2),Y(2),A(6)SCH
EQUIVALENCE(D,FELT(1)),(X,E1),(Y,E2),(A,E3),(Z,ENERG),(Z,FELT(7))SCH
EQUIVALENCE(DELT,FELT(25))SCH
EQUIVALENCE (MSPARE,ID)SCH
EQUIVALENCE (IO,LSPARE)SCH
EQUIVALENCE (ITAG(5),PA)SCH
DIMENSION AG(2)SCH
1984 DATA ( AG(1),1,1,2)/6HOVRLAP,6HHAMILT/SCH
109 FORMAT(13X, 5HFPAR(12,1H,12,2H)=F10.5,4X,4HNCL=I5)SCH
104 FORMAT(1H0,10HPARAMETERS /)SCH
105 FORMAT(5X,13,2F12.6,3X,6I3)SCH
106 FORMAT(1H0,(13X,7E15.7))SCH
107 FORMAT(1H0,10X,3HE =E16.8,7H FCN(12,1H,12,7H) KOR=I3,SCH
*8H STEPS 2F14.6)SCH
305 FORMAT(1H0,20X,A6,1X,6HMATRIX)SCH
DO 101 I=1,NMATSCH
DO 101 J=1,I
OVP(I,J)=OVRLAP(I,J)SCH
OVP(J,I)=OVRLAP(I,J)SCH

```

C
C
C
C


```

OVR LAP(J,I)=OVR LAP(I,J)
HAM(I,J)= HAMILT(I,J)
HAM(J,I)= HAMILT(I,J)
101 HAMILT(J,I)=HAMILT(I,J)
WRITE(IO,104)
DO 110 J=1,NFCN
110 WRITE(IO,105)J,FPAR(1,J),FPAR(2,J),(NFPAR(I,J),I=1,6)
E2(1)=0.
CALL D23CHO(NMAT,OVP ,HAM ,COET,COETO,E,E2,ID)
NE1=NE+1
IF(EFIN.EQ.0.) GO TO 1000
IF(E(NE1).GT.EFIN) GO TO 1000
WRITE(IO,1003)
1003 FORMAT(1H020X,14HENERGY.LT.MIN.)
GO TO 531
1000 CONTINUE
WRITE(IO,106)(E(I),I=1,NMAT)
WRITE(IO,107)E(NE1),NO,MO,KOR,STEP1,STEP2
1005 GO TO (200,400,262,200), ITX
200 CONTINUE
IF(KR.NE.0) GO TO 2
KR$KW
KW$KOR
GO TO 3
2 KO$KR
KR$KW
KW$KO
3 N10=N
412 EO=E(NE1)
IF(NPC.EQ.0) GO TO 53
KO$ MO=NFCN/2
IF(NOTRF.EQ.1) KO=MO*(NFCN-NU)/2
WRITE(IO,305) AG(1)
CALL PMA(OVR LAP,NMAT,E3,0,E,ID,IO)
WRITE(IO,305) AG(2)

```

```

SCH 360
SCH 370
SCH 380
SCH 390
SCH 400
SCH 410
SCH 420
SCH 430
SCH 440
SCH 450
SCH 460
SCH 470
SCH 480
SCH 490
SCH 500
SCH 510
SCH 520
SCH 530
SCH 540
SCH 550
SCH 560
SCH 570
SCH 580
SCH 590
SCH 600
SCH 610
SCH 620
SCH 630
SCH 640
SCH 650
SCH 660
SCH 670
SCH 680
SCH 690
SCH 700

```



```

CALL PMA(HAMILT,NMAT,E3.0,E.ID,IO)
ITX#2
KOR=0
GO TO 401
400 KO= MO*NFCN/2
IF(NOTRF.EQ.1) KO=MO+(NFCN-NU)/2
IF(E(NEL).GE.E0) GO TO 401
MU=KR
KR=KW
KW=MU
FPARO(NO,MO)=FPAR(NO,MO)
IF(ITAG(4).NE.0) FPARO(NO,KO )=FPAR(NO,KO )
EO=E(NEL)
401 KOR=KOR+1
CALL SSWTCH(4,IREX)
IF(IREX.EQ.2) GO TO 403
RMAX#RMIN
LIAR#1
GO TO 62
403 IF(LSRCH.EQ.0) GO TO 402
C LINEAR STEP SEARCH ONLY
IF(KOR.EQ.LSRCH) GO TO 804
805 FPAR(NO,MO)=FPAR(NO,MO)+STEP1
GO TO 11
804 FPAR(NO,MO)=FPARO(NO,MO)
GO TO 40
402 CONTINUE
CALL SSWTCH(5,IREX)
IF(IREX.EQ.1) GO TO 998
ENERG(KOR) = E(NEL)
IF((NO.EQ.2).AND.(IS.LE.1)) GO TO 500
1500 D(KOR)=FPAR(NO,MO)
GO TO (10,20,31,540), KOR
C DELTA SEARCH
10 PA=1.

```

SCH 710
SCH 720
SCH 730
SCH 740
SCH 750
SCH 760
SCH 770
SCH 780
SCH 790
SCH 800
SCH 810
SCH 820
SCH 830
SCH 840
SCH 850
SCH 860
SCH 870
SCH 880
SCH 890
SCH 900
SCH 910
SCH 920
SCH 930
SCH 940
SCH 950
SCH 960
SCH 970
SCH 980
SCH 990
SCH 1000
SCH 1010
SCH 1020
SCH 1030
SCH 1040
SCH 1050


```

21 FPAR(NO,MO)=D(KOR) + PA*STEP1
11 SIG=1.
   IF((ZA.EQ.ZB).AND.(MOD(NHUG,2).EQ.0)) SIG=-1.
12 IF(FPAR(1,MO).LT.0.01) FPAR(1,MO)=.01
   IF(ABS(FPAR(2,MO)).GT.1.1*FPAR(1,MO)) FPAR(2,MO)=SIGN(1.1*FPAR(1,MO),
      *O).FPAR(2,MO))
   IF(ITAG(4).EQ.0) GO TO 241
   FPAR(1,KO)=FPAR(1,MO)
   FPAR(2,KO)=SIG*FPAR(2,MO)
241 RETURN
20 IF(Z(2).LT.Z(1)) GO TO 21
   PA=-1.
   FPAR(NO,MO)=D(1) + PA*STEP1
   GO TO 11
31 IF(Z(3).GT.E0) GO TO 30
   IF(ABS(FPAR(NO,MO)).LT.0.011) GO TO 30
   IF(ABS(FPAR(2,MO)).GT.(1.09*FPAR(1,MO))) GO TO 30
33 Z(1)=Z(2)
   Z(2)=Z(3)
   D(1)=D(2)
   D(2)=D(3)
   KOR=2
   PA=1.5*PA
   GO TO 21
30 A(5)=0.
   DO131 I=1,3
     X(I)=D(I)*D(I)
     Y(I)=D(I)
131 CONTINUE
     A(1)=Z(1)*(Y(2)-Y(3))+Y(1)*(Z(3)-Z(2))+Z(2)*Y(3)-Y(2)*Z(3)
     A(2)=X(1)*(Z(2)-Z(3))+Z(1)*(X(3)-X(2))+X(2)*Z(3)-Z(2)*X(3)
     DELT=-.5*A(2)/A(1)
     WRITE(10,109) NO,MO,DELT,NC1
     IF(A(1)/(D(1)-D(2))*(D(1)-D(3))*(D(2)-D(3)))) 35,999,32
32 FPAR (NO,MO)=DELT

```

SCH 1060
 SCH 1070
 SCH 1080
 SCH 1090
 MSCH 1100
 SCH 1110
 SCH 1120
 SCH 1130
 SCH 1140
 SCH 1150
 SCH 1160
 SCH 1170
 SCH 1180
 SCH 1190
 SCH 1200
 SCH 1210
 SCH 1220
 SCH 1230
 SCH 1240
 SCH 1250
 SCH 1260
 SCH 1270
 SCH 1280
 SCH 1290
 SCH 1300
 SCH 1310
 SCH 1320
 SCH 1330
 SCH 1340
 SCH 1350
 SCH 1360
 SCH 1370
 SCH 1380
 SCH 1390
 SCH 1400


```

DO 34 I=1,3
IF (ABS(DELT-D(I)).LT.1.E-5) GO TO 40
34 CONTINUE
GO TO 11
999 NFPAR(6,MO)=1
IF (NO.EQ.2) NFPAR(6,MO)=2
40 KOR=1
PA=1.
Z(1)=EO
FPAR(NO,MO)=FPAR(NO,MO)
IF (ITAG(4).NE.0) FPAR(NO,KO )=FPAR(NO,KO )
41 IF (NO.EQ.2) GO TO 60
IF (NFPAR(6,MO).GE.2) GO TO 60
NO=NO+1
D(1)=FPAR(NO,MO)
IF (IS.GT.1) GO TO 10
INITIAL ALPHA SEARCH
500 GO TO (510,520, 30,540), KOR
510 D(3)=D(1)/2.
D(2)=D(1)+D(3)
FPAR(NO,MO)=D(2)
GO TO 11
520 FPAR(NO,MO)=D(3)
GO TO 11
540 NC2P=0
DO 541 I=1,4
IF (ABS((Z(1)-Z(4))/Z(4)).LT.1.E-5) NC2P=NC2P+1
541 CONTINUE
C SET TAG IF ENERGY IS INDEPENDENT OF PARAMETER
IF (NC2P.EQ.4) NFPAR(6,MO)= NO + NFPAR(6,MO)
GO TO 40
60 IF (MO.EQ.NPC) GO TO 61
MO=MO+1
KO=KO+1
NO =1
SCH 1410
SCH 1420
SCH 1430
SCH 1440
SCH 1450
SCH 1460
SCH 1470
SCH 1480
SCH 1490
SCH 1500
SCH 1510
SCH 1520
SCH 1530
SCH 1540
SCH 1550
SCH 1560
SCH 1570
SCH 1580
SCH 1590
SCH 1600
SCH 1610
SCH 1620
SCH 1630
SCH 1640
SCH 1650
SCH 1660
SCH 1670
SCH 1680
SCH 1690
SCH 1700
SCH 1710
SCH 1720
SCH 1730
SCH 1740
SCH 1750

```



```

IF((NFPAR(6,MO).EQ.1).OR.( NFPAR(6,MO).GE.3))      GO TO 41
D(1)=FPAR(NO,MO)
GO TO 10
61 IF(STEP1.LE.STEP2) GO TO 62
STEP1=.3*STEP1
IF(STEP1.LT.STEP2) STEP1=STEP2
LSRCH=0
65 IS=IS+1
64 MO=1
NO = 1
IF(NOTRF.EQ.0) NU=0
MO=MO+NU
KO=(NFCN-NU) /2 +1
D(1)=FPAR(NO,MO)
GO TO 10
62 ITX=3
DO 63 I=1,2
DO 63 J=1,16
63 FPAR(I,J)=FPARO(I,J)
RETURN
262 CONTINUE
53 CONTINUE
531 ITX=0
RETURN
35 WRITE(10,108)
108 FORMAT(1H020X,17HGR.SRCH SEEKS MAX )
GO TO 40
997 FORMAT(1H010X,15HEND SRCH OF FCN 214//)
998 WRITE(10,997) NO,MO
C THIS CANNOT BE DONE ON IBM 7094
PAUSE 998
NFPAR(6,MO)=NO + NFPAR(6,MO)
GO TO 40
END
SCH 1760
SCH 1770
SCH 1780
SCH 1790
SCH 1800
SCH 1810
SCH 1820
SCH 1830
SCH 1840
SCH 1850
SCH 1860
SCH 1870
SCH 1880
SCH 1890
SCH 1900
SCH 1910
SCH 1920
SCH 1930
SCH 1940
SCH 1950
SCH 1960
SCH 1970
SCH 1980
SCH 1990
SCH 2000
SCH 2010
SCH 2020
SCH 2030
SCH 2040
SCH 2050
SCH 2060
SCH 2070
SCH 2080
SCH 2090

```



```

SUBROUTINE D23CHO (N,S,H,P,C,E,NN,ID)
  SOLVES GENERAL SECULAR EQUATION (H-E S)=0 WHERE S NEED NOT BE DIAGONAL
  AL BY CHOLESKY-BANACHIEWICZ ALGORITHM
  IF NN(1) IS SET TO 1313 PRIOR TO ENTRY, PROGRAM DETERMINES LINEAR
  TRANSFORMATION TO ORTHONORMALIZE BASIS SET WHOSE GRAM DETERMINANT
  IS STORED IN ARRAY NAMED S
  DIMENSION S(10,10),H(ID,ID),P(ID,ID),C(ID,ID),E(ID),NN(ID)
  EQUIVALENCE (NT,L),(NTA,K)
  120 FORMAT(1H020X,18H0VRLAP NOT POS DEFE15.7.214)
  IF(N.GT.1) GO TO 100
  E(1)=H(1,1)/S(1,1)
  P(1,1)=1.
  RETURN
  CALCULATE UPPER TRIANGULAR MATRIX
  100 DO 10 J=1,N
    L = J-1
    DO 10 J=1,N
      HH = S(I,J)
      IF(L.EQ.0) GO TO 5
      3 DO 4 K=1,L
        4 HH = HH - S(K,J)*S(K,I)
      5 IF(I.EQ.J) GO TO 7
      6 S(I,J) = HH/S(I,I)
      GO TO 10
      7 IF(HH.GT.1.E-5) GO TO 75
  C IBM COMMON/SPACE/KLUTZ(309)
  C IBM EQUIVALENCE (IOUT,KLUTZ(22))
  C IBM WRITE(IOUT,120) HH,I,J INSTEAD OF PRINT STATEMENT
  PRINT 120, HH,I,J
  IF(HH.GT.0.) GO TO 75
  IF(NN(1).EQ.1313) CALL EXIT
  IF(ABS(HH).LT.1.E-7) GO TO 74
  CALL EXIT
  74 DO 30 K=1,N
    S(I,K) = 0.

```



```

CHO 360
CHO 370
CHO 380
CHO 390
CHO 400
CHO 410
CHO 420
CHO 430
CHO 440
CHO 450
CHO 460
CHO 470
CHO 480
CHO 490
CHO 500
CHO 510
CHO 520
CHO 530
CHO 540
CHO 550
CHO 560
CHO 570
CHO 580
CHO 590
CHO 600
CHO 610
CHO 620
CHO 630
CHO 640
CHO 650
CHO 660
CHO 670
CHO 680
CHO 690
CHO 700

```

```

      S(K,I) = 0.
      H(K,I) = 0.
30  H(I,K) = 0.
      S(I,I) = 1.0E-10
      H(I,I) = 1.0E+5
      GO TO 10
75  S(I,J) = SORT(HH)
10  CONTINUE
      INVERSE MATRIX    IN UPPER TRIANGLE
      DO 18 J=1,N
        L = J-1
        DO 18 I=1,N
          IF(I-J) 12,11,20
20  S(I,J) = 0.
          GO TO 18
11  S(J,J) = 1.0 / S(J,J)
          GO TO 18
12  HH = 0.
13  DO 14 K=1,L
14  HH = HH-S(K,J)*S(I,K)
15  S(I,J) = HH/S(J,J)
18  CONTINUE
      IF(NN(1).EQ.1313) RETURN
      TRANSFORM H-MATRIX
      DO 29 I=1,N
        DO 29 J=I,N
          HH = 0.
          DO 28 K=1,I
            DO 27 L=1,J
              HH = HH+S(L,J)*S(K,I)*H(K,L)
27  CONTINUE
28  CONTINUE
          P(J,I) = HH
29  P(I,J) = HH
      CALL EIG(N,P,C,ID)

```



```

N1=N
DO 2 I=1,N1
E(I)=P(I,I)
2 NN(I)=1
IF (N1.EQ.1) GOTO40
NT=N1
NT=NT-1
NTA=0
ORDER EIGENVALUES AND EIGENVECTORS
DO 33 J=1,NT
IF ((E(J+1)-E(J)).GE.0.) GO TO 33
HH=E(J+1)
E(J+1)=E(J)
E(J) = HH
I=NN(J+1)
NN(J+1)=NN(J)
NN(J)=I
NTA=1
33 CONTINUE
IF (NTA.EQ.1) GO TO 1
TRANSFORM C TO P
C 40 DO 21 J=1,N
NT=NN(J)
DO 21 I=1,N
HH=0.
DO 22 K=1,N
22 HH=HH+S(I,K)*C(K,NT)
21 P(I,J) = HH
RETURN
END
CHO 710
CHO 720
CHO 730
CHO 740
CHO 750
CHO 760
CHO 770
CHO 780
CHO 790
CHO 800
CHO 810
CHO 820
CHO 830
CHO 840
CHO 850
CHO 860
CHO 870
CHO 880
CHO 890
CHO 900
CHO 910
CHO 920
CHO 930
CHO 940
CHO 950
CHO 960
CHO 970
CHO 980
CHO 990
CHO 1000

```



```

SUBROUTINE      EIG  (N,H,C,ID)
C  FINDS EIGENVALUES AND COLUMN EIGENVECTORS BY JACOBI METHOD
C  INPUT MATRIX IS H, EIGEN VALUES RETURNED IN H(I,I)
C  VECTOR MATRIX IS C, SET TO IDENTITY MATRIX IN THIS ROUTINE
C  DIMENSION H(ID,ID),C(ID,ID)
C  IF(N.EQ.1) RETURN
C  ENTER UNITY-MATRIX
DO 99 I1=1,N
DO 98 J1=1,N
98 C(I1,J1)=0.
99 C(I1,I1)=1.
SIG=N*N
TR=0.
DO 1 I1=2,N
M=I1-1
DO 1 J1=1,M
H(J1,I1)=H(I1,J1)
TR=TR+ABS(H(I1,J1))
1 IF(TR.EQ.0.) RETURN
SUM=TR
THRESH=1.E-15*TR
105 TR=SUM/SIG
107 LTAG=0
SUM=0.
M=N-1
KKK=0
DO 137 K=1,M
KKK=KKK+1
L=K+1
DO 137 J1=KKK,K
DO 137 I1=L,N
SUM=SUM+ABS(H(I1,J1))
115 IF(ABS(H(I1,J1)).LE.TR) GO TO 137
LTAG=L
P=L.
EIG 10
EIG 20
EIG 30
EIG 40
EIG 50
EIG 60
EIG 70
EIG 80
EIG 90
EIG 100
EIG 110
EIG 120
EIG 130
EIG 140
EIG 150
EIG 160
EIG 170
EIG 180
EIG 190
EIG 200
EIG 210
EIG 220
EIG 230
EIG 240
EIG 250
EIG 260
EIG 270
EIG 280
EIG 290
EIG 300
EIG 310
EIG 320
EIG 330
EIG 340
EIG 350

```



```

X=H(I1,J1)
CC=.5*(H(I1,I1)-H(J1,J1))
IF(CC.LI.0.) P=P
P=P*X/SQRT(X*X+CC*CC)
CC=SQRT(1.-P*P)
S=P/SQRT(2.*(1.+CC))
SS=S*S
CC=1.-SS
X=SQRT(CC)
S2=2.*X*S
TRANSFORM 2X2 BLOCK
P=H(I1,I1)+H(J1,J1)
CC =H(I1,I1)*CC-H(I1,J1)*S2+H(J1,J1)*SS
SS=P-CC
DO 242 JP=1,N
P=H(I1,JP)
H(I1,JP)=P*X-H(J1,JP)*S
H(J1,JP)=P*S+H(J1,JP)*X
H(JP,I1)=H(I1,JP)
H(JP,J1)=H(J1,JP)
P=C(JP,I1)
C(JP,I1)=P*X-C(JP,J1)*S
C(JP,J1)=P*S+C(JP,J1)*X
242 CONTINUE
H(I1,I1)=CC
H(J1,J1)=SS
H(J1,I1)=0.
H(I1,J1)=0.
137 CONTINUE
IF(LTAG.EQ.1) GO TO 107
IF(SUM.GT.THRESH) GO TO 105
RETURN
END

```

C

EIG 360
 EIG 370
 EIG 380
 EIG 390
 EIG 400
 EIG 410
 EIG 420
 EIG 430
 EIG 440
 EIG 450
 EIG 460
 EIG 470
 EIG 480
 EIG 490
 EIG 500
 EIG 510
 EIG 520
 EIG 530
 EIG 540
 EIG 550
 EIG 560
 EIG 570
 EIG 580
 EIG 590
 EIG 600
 EIG 610
 EIG 620
 EIG 630
 EIG 640
 EIG 650
 EIG 660
 EIG 670
 EIG 680


```

C      SUBROUTINE      PMA  (A,N,NN,NBOOL,E,ID,KU)
C      PRINTS MATRICES AND ARRAYS
C      NBOOL = 0 SYMMETRIC, PRINT LOWER TRIANGLE
C      NBOOL = 1 UNSYMMETRIC MATRIX, E(I) IS NOT PRINTED
C      NBOOL = 2 UNSYMMETRIC MATRIX, PRINT OF VECTOR E
C      KU= IDENT. OF COMMON OUTPUT DEVICE(TAPE,DISC)
C      DIMENSION A(ID,ID),NN(ID),E(ID)
101  FORMAT(1H0,10X,7(110,5X) )
102  FORMAT(17,3X,7E15,7)
103  FORMAT (//)
104  FORMAT (10X,7E15,7)
      DO 13 I=1,N
13  NN(I) = I
      LPM = 7
      DO 8 JA = 1,N,LPM
      JE = JA+LPM-1
      IF (N.LT.JE) JE = N
3  WRITE(KO,101)(NN(J),J=JA,JE)
      WRITE(KO,103)
      IF (NBOOL .LT.2) GO TO 15
      WRITE(KO,104)(E(J),J=JA,JE)
      WRITE(KO,103)
15  L = JA
      IF (NBOOL .NE. 0) L=1
      DO 7 I=L,N
      IE = JE
      IF (NBOOL.NE.0) GO TO 6
      IF (I.LT.JE) IE=I
7  WRITE(KO,102)NN(I),(A(I,J),J=JA,IE)
8  CONTINUE
      CONTINUE
      RETURN
      END
PMA 10
PMA 20
PMA 30
PMA 40
PMA 50
PMA 60
PMA 70
PMA 80
PMA 90
PMA 100
PMA 110
PMA 120
PMA 130
PMA 140
PMA 150
PMA 160
PMA 170
PMA 180
PMA 190
PMA 200
PMA 210
PMA 220
PMA 230
PMA 240
PMA 250
PMA 260
PMA 270
PMA 280
PMA 290
PMA 300
PMA 310
PMA 320
PMA 330

```



```

C      SUBROUTINE OUTPUT (LCON,NUMBR,NEL)
C      CONTROLLING PROGRAM OF OUTPUT      BRANCH
C      PRINTS FINAL OUTPUT
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
      1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,OUT
      2LSRCH,JKW3,LIAR,STEP1,STEP2,E0,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)OUT
      3,FPAR0(2,16),FPAR(2,16),NFPAR(6,16),ITAG( 6),ICTAG(64),
      4DELT(25),RMAX,RMIN,KSTEP,STEP3
      COMMON/WORK/OVR LAP(42,42),HAMILT(42,42),COET(42,42),COETO(42,42),
      *OLP(42,42),HAM(42,42),E(42),E4(42,6),A,1,J,K,L,M,L1,L2,I7,I6,I5,
      1BLANK,TAGIT,F(1627)
      COMMON/CIJ/C(16,16),NOTRF,EUGEN(11)
      DIMENSION PROD(30),TAG(6)
      EQUIVALENCE (PROD,F)
      EQUIVALENCE (JO,LSPARE)
      DIMENSION LCON(NUMBR,NEL)
      SQRTF(X)=SQRT(X)
      999 DATA (TAG(1),1=1,6)/1H,1HG,1HU,6HHAMILT,6HOVR LAP,6HTRANS, /
      305 FORMAT(1H0,20X,A6,1X,6HMATRIX)
      300 FORMAT( //30H PARAMETERS FOR CONFIGURATION,I3,/ )
      301 FORMAT(12H ELECTRON,I3,F11.5,F11.5,3I7.6X,A1)
      302 FORMAT(21X,48HDELTA ZETA N M NU PARITY )OUT
      312 FORMAT(14H ENERGY=,1PE14.7,6H NE=,I2,/ )
      314 FORMAT(1H0,10X,31HENERGIES(ELECTRONIC + NUCLEAR) 24X,21HDISSOCIATION
      1ON ENERGIES / 2(17X,23HHARTREES ELECT. VOLTS6X,9HKCAL/MOLE) /)
      315 FORMAT(2(10X,3E15.7))
      320 FORMAT(/ 7X,23HNORMALIZED COEFFICIENTS )
      321 FORMAT (/7X,12HCOEFFICIENTS )
      1313 FORMAT(1H0,30X, 55HTHE MONSTER - COURTESY OF KEN WILLIAMS AND EUGEN
      *N WELTIN /)
      WRITE(IO,1313)
      N1=NMAT
      N10=N1
      A=ZA*ZB/R
      DO 500 I=1,NMAT
      10 OUT
      20 OUT
      30 OUT
      40 OUT
      50 OUT
      60 OUT
      70 OUT
      80 OUT
      90 OUT
      100 OUT
      110 OUT
      120 OUT
      130 OUT
      140 OUT
      150 OUT
      160 OUT
      170 OUT
      180 OUT
      190 OUT
      200 OUT
      210 OUT
      220 OUT
      230 OUT
      240 OUT
      250 OUT
      260 OUT
      270 OUT
      280 OUT
      290 OUT
      300 OUT
      310 OUT
      320 OUT
      330 OUT
      340 OUT
      350 OUT

```



```

E4(I,1)=E(I)+A
E4(I,2)=E4(I,1)*27.21
E4(I,3)=E4(I,1)*627.71
E4(I,4)=E4(I,1)-A1-A2
E4(I,5)=E4(I,4)*27.21
500 E4(I,6)=E4(I,4)*627.71
DO 54 K = 1,N10
54 PROD(K)=0.
L2 = NMAT-1
DO 55 K=1,N10
DO 55 L1 = 1,L2
L = L1+1
DO 55 M= L,NMAT
55 PROD(K)= PROD(K) + 2.*(COET(L1,K)*COET(M,K)*OVR LAP(M,L1))
DO 56 K=1,N10
DO 56 L=1,NMAT
56 PROD(K) = PROD(K)+COET(L,K)**2 *OVR LAP(L,L)
DO 57 K=1,N10
DO 57 L=1,NMAT
IF(OVR LAP(I,1).GE.0.) GO TO 57
OVR LAP(I,1)=0.
57 COET0(I,K)=(COET(I,K)/SQRTF(PROD(K)))*SQRTF(OVR LAP(I,1))
C
OUTPUT
CALL HDG
WRITE(10,312) EO,NE
DO 350 I5=1,NCON
WRITE(10,300) I5
WRITE(10,302)
DO 351 I6=1,N
I7=LC ON(I5,I6)
BLANK=TAG(1)
IF(MOD(NHUG,2).EQ.0) GO TO 996
BLANK=TAG(2)
IF(NFPAR(4,I7).NE.0) BLANK=TAG(3)
996 WRITE(10,301) I7,FPAR (1,I7),FPAR (2,I7),(NFPAR (L,I7),L=1,3),BLANKOUT

```

OUT 360
OUT 370
OUT 380
OUT 390
OUT 400
OUT 410
OUT 420
OUT 430
OUT 440
OUT 450
OUT 460
OUT 470
OUT 480
OUT 490
OUT 500
OUT 510
OUT 520
OUT 530
OUT 540
OUT 550
OUT 560
OUT 570
OUT 580
OUT 590
OUT 600
OUT 610
OUT 620
OUT 630
OUT 640
OUT 650
OUT 660
OUT 670
OUT 680
OUT 690
OUT 700


```

351 CONTINUE
350 CONTINUE
    WRITE(10,320)
    CALL PMA(COET0,NMAT,F,2,E4(1,1),MSPARE,10)
    CALL HDG
    WRITE(10,314)
    WRITE(10,315)((E4(1,J),J=1,6),I=1,NMAT)
    CALL HDG
    WRITE(10,305) TAG(5)
    CALL PMA(OVRLAP,NMAT,F,0,E,MSPARE,10)
    WRITE(10,305) TAG(4)
    CALL PMA(HAMILT,NMAT,F,0,E,MSPARE,10)
    WRITE(10,321)
    CALL PMA(COET,NMAT,F,2,E,MSPARE,10)
    IF(NOTRF.EQ.0) RETURN
    WRITE(10,305) TAG(6)
    CALL PMA(C,NFCN,F,1,F,16,10)
    RETURN
    END
♦)-P0.CE

```

```

OUT 710
OUT 720
OUT 730
OUT 740
OUT 750
OUT 760
OUT 770
OUT 780
OUT 790
OUT 800
OUT 810
OUT 820
OUT 830
OUT 840
OUT 850
OUT 860
OUT 870
OUT 880
OUT 890

```


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